Development of Organic Solute Concentration Profile Within Micelle for Micellar Enhanced Ultrafiltration Studies

A Thesis Submitted in Partial Fulfilment of the Requirements for the Degree of
MASTER OF TECHNOLOGY

by

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to the

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CERTIFICATE

This is to certify that the work entitled, **"DEVELOPMENT OF ORGANIC SOLUTE CONCENTRATION PROFILE WITHIN MICELLE FOR MEUF STUDIES"**, by **Manoranjan Syamal** has been carried out under my supervision and that has not been submitted elsewhere for Degree.

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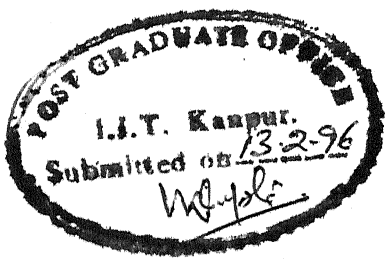

DEDICATED TO

MY

PARENTS

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ABSTRACT :

An attempt has been made to analyse the distribution of organic solute within micelle. Experiments were carried out both stirred and unstirred cell, using asymmetric cellulose acetate membrane of 1000 molecular weight cut off. The solute and surfactant were taken PhOH and CPC respectively. For a particular experimental condition flux was constant. There is a distribution of organic solute between aqueous phase and micelle phase. The solute consumption capacity of the micelle decreases with increase in pressure. With increase in surfactant concentration the percentage consumption of organic solute increases but observe rejection of the surfactant with respect to membrane decreases, which is not desirable for industrial applications. Therefore, there must be some optimal surfactant/solute ratio in which micelle enhanced ultrafiltration works most efficiently.

Recovery of surfactant made possible by adopting a standard procedure. Hence, the MEUF processes will be cost saving.

Contents

NOMENCLATURE :

a = Area per head group (m^2). Pore radius (m)

A = Membrane surface area (m^2)

C = Solute concentration(kg/m^3)

C = Solute concentration (kg/m^3)

C_b = Bulk concentration (kg/m^3)

C_m = Membrane surface solute concentration (kg/m^3)

C_p = Permeate concentration (kg/m^3)

D = Diffusivity (m^2/s), optical density

G = Free energy per mole ($J/mole\epsilon$)

H= Enthalpy ($j/mole\epsilon$), equilibrium parameter

J = Flux (m/s)

K = Apparent solubilisation constant

K_1, K_2 = Integration constants

l = Cell thickness (m)

P = Pressure (Pa)

r_0 = Interior space of the micelle (m)

R =Radius (m), Gas constant (J/(mole.K))

R_a = Resistance due to adsorption (m^{-1})

R_m = Membrane resistance (m^{-1})

R_o = Observe rejection

R_p = Resistance due to polarisation (m^{-1})

R_r = Real rejection

S =Entropy (J/K)

t = Time (s)

T = Absolute temperature (K)

ABBREVIATIONS :

amp = Amper

cmc = Critical micelle concentration

conc. = Concentration

Hz = Hertz

m = Monomer

M = Micelle

MWCO = Molecular weight cut-off

n = Aggregation number

nm = Nanometer

ppb = Parts per billion

rpm = Revolution per minute

v = Volt

w = Watt

X = Mole fraction

GREEK LETTERS :

μ_m = Viscosity of the solution $(kg/m.s)$

τ = Tortuosity

δ = Membrane thickness

π = Osmotic pressure

Θ, ϕ = Spherical coordinate

ϕ_s = Mole fraction of micelle

SUPERSCRIPTS :

o = Standard state

- = Average

SUBSCRIPTS :

1 = Solvent

2 = Solute

c = Colligative

Chapter 1

INTRODUCTION :

One of the most benful problems confronting chemical engineers and separating scientists is he removal of toxic organic materials present in small or trace quantity from aqueous solutions. Membrane separation processes while attracting in principle, are not technically viable. Membranes capable of passing water but rejecting small organic molecules are simply not now available. Extensive research is getting carried out world wide to develop membranes particularly ceramics membranes or inorganic membrane to fulfill this inadequacy. Till much success is yet to come. The process most conventionally adopted is fixed bed adsorption. However, this procedure is neither selective nor particularly energy efficient. Other alternatives such as distillation or solvent extraction are apparently even more unattractive.

Micelle enhanced ultrafiltration (MEUF) is a recent develop technique that remove dissolved organic solute from water. In this proposed process [1-2] surfactant is added to the water stream. The surfactant forms spheroidal aggregates of about 50-150 molecules called micelles. The original organic solute tends to solubilize or dissolved in the interior of the micelles. Some selectivity is possible because the extent of solubilisation will depend on both the structure of the solubilizate and the surfactant. The micellar solution is filtered through a membrane capable of rejecting micelles. The solubilizate is, therefore, also rejected. The retentate contains the rejected organic solubilizate and the surfactant. Scamehorn et al. [1-2] termed this process as MEUF. The process is versatile enough to

include separation of hydrocarbon, recovery and removal of organic acids and amines, and separation and concentration of metal ions. Hence addition of surfactant above its critical micelle concentration (cmc) to water containing dilute hydrophobic organic pollutants can be removed in solubilization of the solute in the micellar interior. A schematic version of MEUF process is shown in fig. 1.1.

In theory, the concentration of solute in the permeate stream should be equal to or less than the unsolubilized solute concentration in the retentate. The theoretical surfactant concentration should be equal or less than the monomeric surfactant concentration in the retentate. Both these concentrations can be very low, resulting in very pure permeate. The retentate stream contains the solubilized solute and the surfactant (in micellar form) in very high concentrations. This stream is much smaller in volume than the original feed stream so is much less expensive to dispose off or to treat to recovery the solute and surfactant. Since the surfactant and solute generally have vastly different physical properties, they can be separated quite readily.

The selection of a surfactant is an important issue in in designing separation processes based on MEUF. The binding of hydrophobic solutes to both ionic and nonionic micelles was considered and was shown to be a function of the molecular structure of the surfactants, the concentration of the surfactant and the electrolytic composition of the water [3]. However, the present work was not started with this aim. Further many work has come in this direction. Several models have been attempted to predict and to provide understanding behind the movement and attachment between the solute and the micelles. Markel et al. [4] have recently studied micellar ultrafiltration in an unstirred batch cell at constant flux. They have developed an unsteady mass-transfer model to describe MEUF at constant flux and claimed excellent agreement between the model and experiment. The model is able to describe quantitative characterization of the intrinsic membrane rejection properties for both surfactant monomer and micelles, and support

the physics at the membrane surface (presumed in the model). However, such surfaced based model may not able to describe the complete physics until what happens in the interior of the micelles is also understood. Since, micelles vary in shape and sizes, an assumption may be taken where solute once comes on to the surface of the micelles enter into the interior[5]. Such assumed physics may allow us to incorporate the mass transfer phenomena in the interior of the micelles. Such attempts have not been made elsewhere, hence, the present work has been under taken to study micellar enhanced ultrafiltration in a batch cell at constant flux with the assumed physics stated above. Further in predicting MEUF separation efficiency it is use to have information about the equilibrium behavior of the particular organic solubilizate species. Such attempts of development of a model is predict MEUF process would help in efficient design and understanding of the processes.

Thus the major broad objectives to remove organic solute dissolved in water by MEUF are:

(1) To carry out an experimental study using different concentration of a particular organic solute (phenol in water) using different concentration of surfactant (cetylpyridinium chloride, cpc) in a stirred and unstirred batch cell at different operating conditions.

(2) To develop a mathematical model using mass-transfer phenomena for the case of a solute present at the surface of the micelle and entering into the micelles.

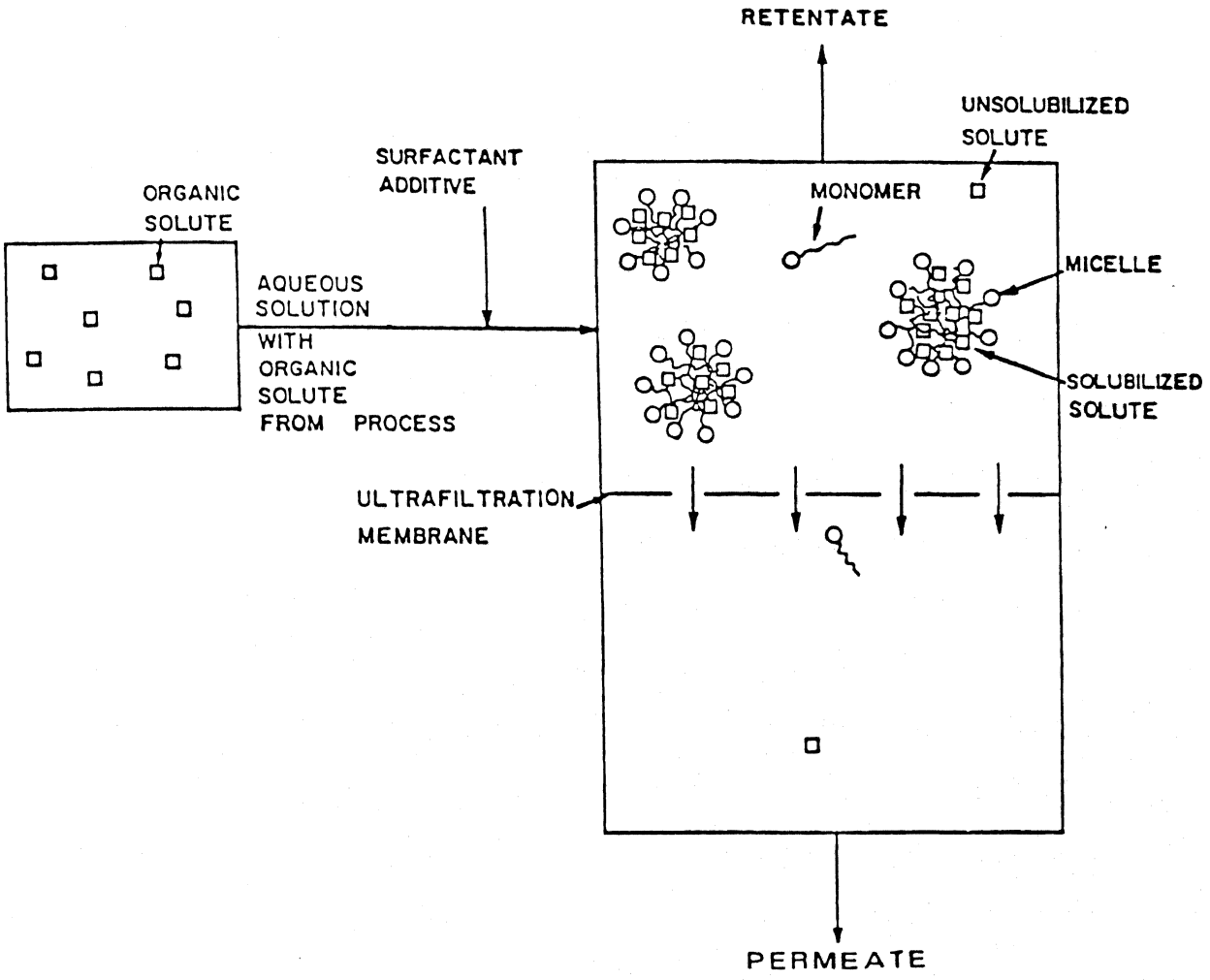


FIG. 1.1 Schematic of micellar-enhanced ultrafiltration to remove dissolved organics from water.

Chapter 2

LITERATURE CITED :

2.1 Separation processes involving organic solute in aqueous medium :

In the petrochemical industries separation processes are employed, in addition to feed stock preparation, for the separation of the desire product, often is very high purity. Among the separation processes, the main processes are; distillation, extraction, adsorption and membrane separation. Although distillation is the oldest separation process it continues to be the main workhorse. There has been a growth of adsorption processes both in the gas and liquid phase in the recent past. Also membrane separation has made an entry in the petroleum industry and several potential areas are being investigated. For removal of volatile organic matters from ground water, an air stripping system using Rigee process was installed in a plant in Michigan in 1985. Organic contaminant are reduced from 300 to 3000 ppb to 1 ppb. Extraction processes are also widely used in the petroleum industries, particularly in two areas 1) in the production of light aromatic, and 2) in the dearomatisation of lube fraction for improvement its viscosity index. Membrane separation has been practiced in many years of liquid-liquid and liquid- solid streams. Only in 1979 membrane separation has been used in gas separations. Pervaporation process has the potential in the following areas. Methanol recovery in MTBE, dewatering of alcohol and solvent, and organic solvent recovery from waste water. Membrane are also being used for gas separation in the following areas: hydrogen recovery, air separation and acid

gas and water removal from natural gas.

2.2 MEUF :

Micellar enhanced ultrafiltration (MEUF) has been shown an effective method for removing water-soluble organic pollutants from aqueous streams. During the last decade lot of work have been carried out in this field. All attempts have been made to describe flux, permeate concentration varying with time and development of different mathematical models. Further,the behavior of micelles on UF membranes with respect to fouling has been also of concern to researchers. Bhat et al. have been shown to be for several type of organic compounds [1,7-8]. In MEUF a surfactant is added to the aqueous stream containing a dissolved organic contaminant, causing a large fraction of the solute to associate with surfactant micelles. When the aqueous stream is passed through an ultrafilter having a molecular weight cut off in the range of 1000-20000, most of the surfactant and the organic compounds remain in the retentate solution. In a number of MEUF experiments, the effluent or permeate solution has been shown to contain organic solute at a very low concentration, approximately equal to the concentration of the free organic molecules in the retentate solution.

2.2.1 Equilibrium solubilisation of organic solute in micelle :

In MEUF solubilisation of organic solute in the micelle combined with ultrafiltration of these micellar solution, lead to the removal of dissolved, low molecular weight, organic pollutant from water. Since permeate and unsolubilised solute have same concentration, the equilibrium solubilisation of the solute dictates the permeate purity and rejection of the solute by the membrane. Studied have been made for the equilibrium solubilisation-different solubilisate o-, m- and p-cresol [8], 1-butanol and 1-pentanol [9], benzoic and

phenylacetic acid [10]. using different micellar solution through out the range of concentrations. To observe the micellisation equilibrium affected by solubilizates [9]. Apparent solubilisation constants have been defined [7-10],

K=(mole fraction of cresol in the micelle)/(conc.of unsolubilised cresol).

K=(solubilised phenol)/(monomeric phenol)(micellarsurfactant).

And have correlated with mole fraction ofsolubilisate within the micelle. The activity co-efficient[9-10] of both solubilisate and surfactant were obtained, consistant with the Gibbs-Duhem equation. The appararent solubilisation constant also decreased appreciably, and the activity co-efficients of the solute increased. as the mole fraction of the solute in the micelle increased.

2.2.2 Selection of surfactants :

Among three different kind of surfactants namely cationic, anionic and nonionic (zwitterionic) the selection of a surfactant is an important issue in designing separation processes based on MEUF [12]. The binding of hydrophillic solutes to both ionic and nonionic micelles was considered and shown to be a function to the molecular structure of the surfactants, concentration of the surfactant, and the electrolytic composition of water. Swelling of the micelle by solubilising certain non polar compounds was found to be only marginally improving the separation efficiency. There appears to be an optimum surfactant molecular structure, but it may not be possible (even under the best conditions) to completely remove any organic solubilisate from it's aqueous streams.

2.2.3 Counter ion binding and mixed micelles :

Micelle composed of mixture of surfactants with different structures (mixed micelles) are of great theoretical and of industrial importance. Since surfactant use in commercial applications are rarely pure, there is increasing interest in understanding the structure and properties of mixed micelles. Example of such applications are enhanced oil recovery and detergency. There has been a great deal of recent effort to model and understand these mixed micelles. However, there is a extreme paucity of data of a key parameter of mixed micelle formation, i.e. counter ion binding. Kamrath and Franses assumed that counter ion binding was constant to their applications of the mass action model to describe mixed micelles [13]. Counter ion binding data can also help to elucidate the physical mechanism leading to non ideality in mixed micelles. For example an ionic/nonionic mixed micelles, the negative deviation from ideality is explained by purely electrostatic arguments, i.e. the reduction in the electrostatic repulsion between charged hydrophillic groups upon insersion of nonionic hydrophilic groups. On the other hand MEUF can be used to separate mono or multivalent ions from the waste streams. For instance, chromate (CrO_4) can be removed from aqueous streams using hexadecylpyridinium chloride as surfactant. Where chromate ions preferentially adsorbed at the surface of the highly charged of the surfactant micelle [14].

2.2.4 Removal of organic pollutants from aqueous streams using MEUF :

MEUF is a membrane separation process which may be used to remove dissolved organic solute from water. In MEUF, surfactant is added to the aqueous stream and form aggregates, called micelles, in to which the solute is solubilizises. The stream is then force through an ultrafiltration membrane with the average pore sizes small enough to reject the micelle containing the solute. The permeate from MEUF contains the organic solute at concentration equal to the unsolubilised solute concentration in the rejected (reten-

tate) solution. The removal of the various organic pollutants, say phenol, benzoic acid, n-hexanol, n-heptanol, n-octanol and o-,m- and p-cresol were studied. Pollutants rejection varied from 75 to 99 percentage, demonstrated the feasibity of the method [9]. Rejection of pollutant increased with increasing hydrocarbon chain length and surfactant/pollutant ratio [10]. On the other hand with increasing surfactant concentration, rejection of surfactant with respect to membrane decreases. Also high flux values were observed.

2.3 NATURE OF SURFACTANT AND MICELLE

2.3.1 Surfactant and micelle :

It is only a technical term, and also diminutive form of the phrase SURFace ACTive AgeNT. Surfactants or surface active agents, are materials that tend not only to accumulate at surfaces, but which by their presence, change the properties of those surfaces. More generally, they are active at interfaces that can be between solid-liquid, liquid-liquid or liquid-gas pairs of phases. However, our major interest, because of their widespread occurrences in natural, industrial and domestic situations, is in systems where the liquid phase is water. Surfactant molecules have two distinct parts, as shown in fig. 2.1a, one that has an affinity to the solvent the other that does not. In aqueous solutions, these two moieties are hydrophilic and hydrophobic respectively. It is the tendency for the hydrophobic parts of the molecules to aggregate because of mutual dislike of the solvent, which is the driving force for surfactant self-association as shown in fig. 2.1b. Micellization occurs when a particular concentration is reached at a given temperature. The initial concentration at which micellization begins is designated as the critical micellization concentration, CMC. Every associate colloid has a definite CMC at a given temperature.

2.3.2 Structure of micelles :

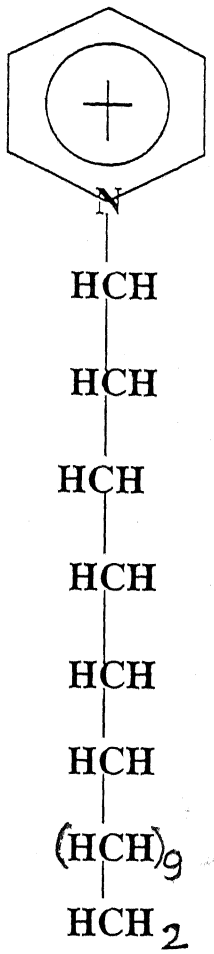
The existence of different shape and size of micelles have been proved [5]. They are vary in shape and size and also interchangeable from one form to another. These are spherical, cylindrical, flexible-bilayer, planer-bilayer and inverted micelles depending upon the conditions of the prevailing systems as shown in fig. 2.2a and 2.2b.

2.3.3 Dynamics of micellar aggregation :

Micelles are not fixed entities but have a transient character. Surfactant monomers rapidly join and leaves the micelles, whose aggregation number present only an average over time. The most widely acceptable method for the determination of aggregation number and size is small angle neutron scattering (SANS).

2.3.4 Micelle formation :

When surfactant molecules are aggregated at the interface, such an oil/water interface, hydrophobic interactions between adjacent alkyl chains provide a force tending to pack the molecules closer together. The hydrophilic groups, on the other hand, have such a strong affinity for water that there is tendency for them to be spaced out to allow as much water as possible to solvate each head group. When the head groups are charged electrostatic repulsion provides an additional force tending to increase the area per molecule. Thus there is a situation of opposing forces, as shown in fig 2.3. Where the interfacial free energy per molecule plotted against, a_o, the area per head group. Hydrophobic interaction tending to decrease the area per molecule where as hydration and electrostatic repulsions are tending to increase the area. The minimum point of the net free energy curve denotes an optimum value for the area per head group a_o. It is assumed that, in any spontaneously formed aggregates, head groups are packed so that they occupy an area very close, a_0.



CETYL PYRIDINIUM CHLORIDE

(CPC)

Fig. 2.1a. Structure of the CPC monomer.

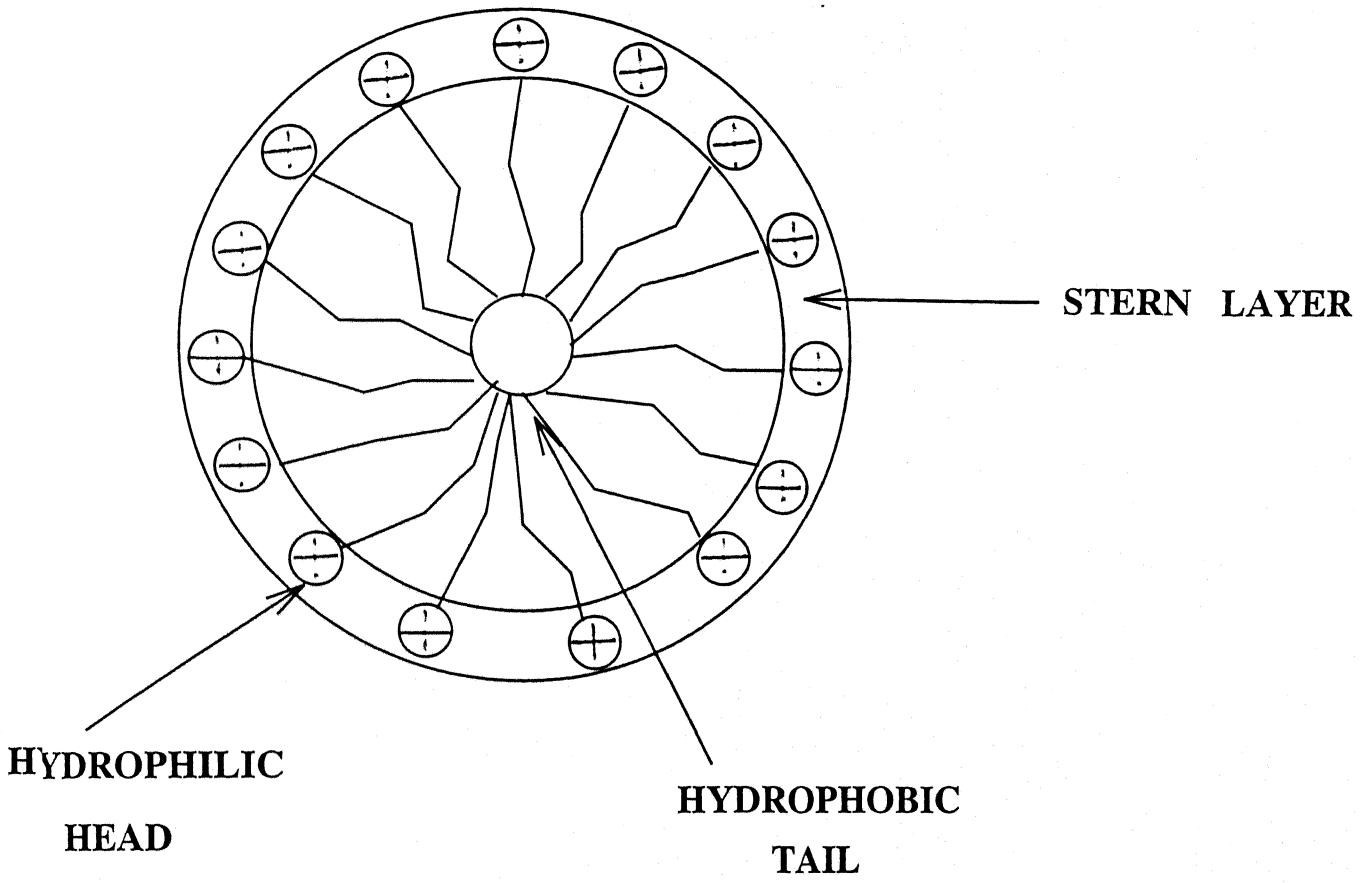


Fig. 2.1b. Probable configuration of a CPC micelle.

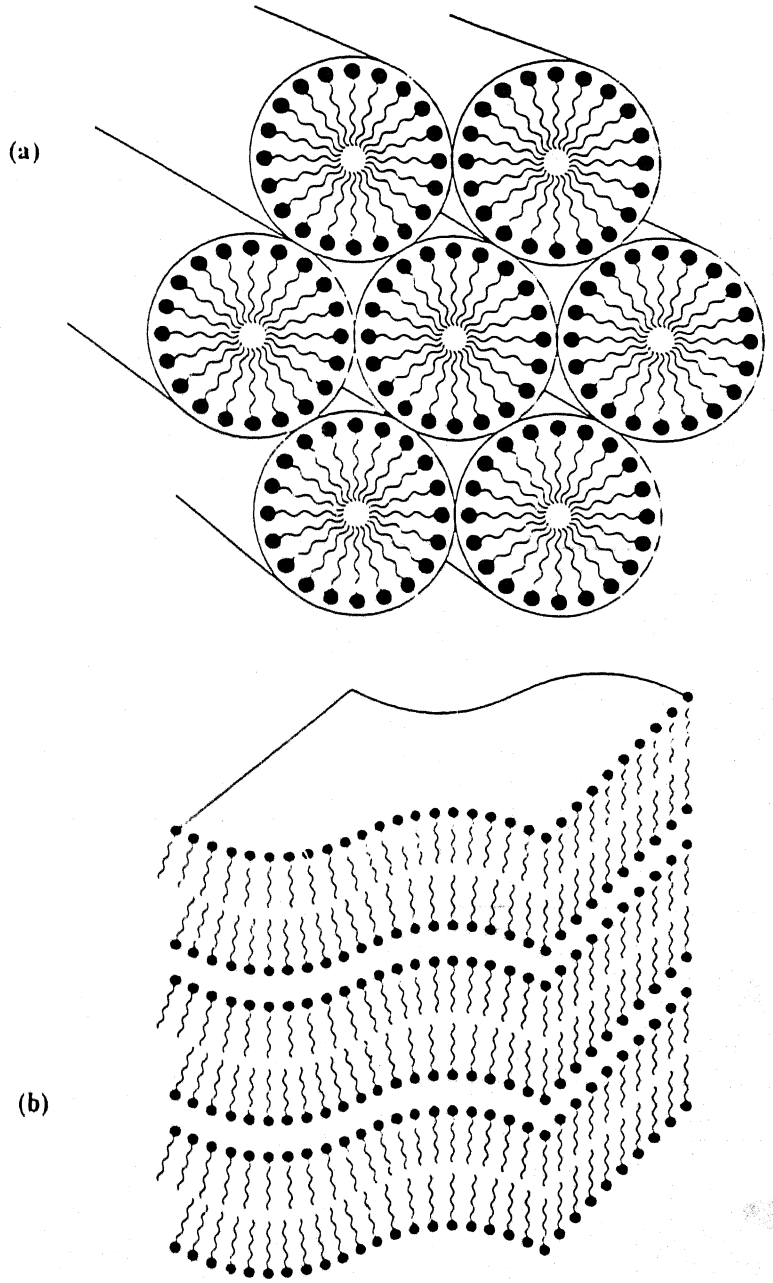
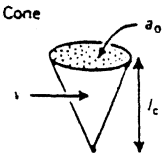
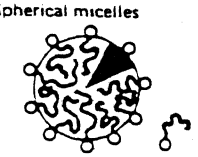
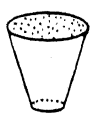
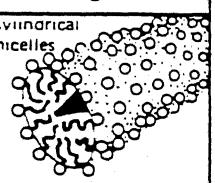
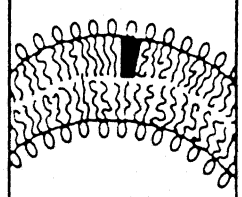
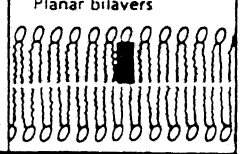
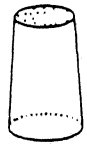
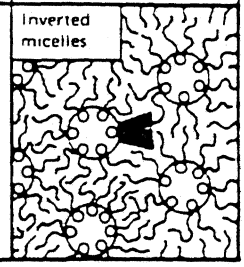


Figure 2.2*a* Schematic drawing of the structure of: (a) the hexagonal liquid-crystalline phase: and (b) the lamellar liquid-crystalline phase.

Lipid	Critical packing parameter $v/a_o l_c$	Critical packing shape	Structures formed
Single-chained lipids (surfactants) with large head-group areas: *SDS in low salt*	< 1/3	Cone 	Spherical micelles 
Single-chained lipids with small head-group areas: *SDS and CTAB in high salt, nonionic lipids*	1/3-1/2	Truncated cone 	Cylindrical micelles 
Double-chained lipids with large head-group areas, fluid chains: *Phosphatidyl choline (lecithin), phosphatidyl serine, phosphatidyl glycerol, phosphatidyl inositol, phosphatidic acid, sphingomyelin, DGDG[a], dihexadecyl phosphate, dialkyl dimethyl ammonium salts*	1/2-1	Truncated cone 	Flexible bilayers, vesicles 
Double-chained lipids with small head-group areas, anionic lipids in high salt, saturated frozen chains: *phosphatidyl ethanolamine, phosphatidyl serine + Ca^{2+}*	~1	Cylinder 	Planar bilayers 
Double-chained lipids with small head-group areas, nonionic lipids, poly *(cis)* unsaturated chains, high T_c *unsat. phosphatidyl ethanolamine, cardiolipin + Ca^{2+} phosphatidic acid + Ca^{2+} cholesterol, MGDG[b]*	> 1	Inverted truncated cone or wedge 	Inverted micelles 

[a] DGDG, digalactosyl diglyceride, diglucosyl diglyceride; [b] MGDG, monogalactosyl diglyceride, monoglucosyl diglyceride.

Figure 2.2b Dependence of aggregate type and geometry on the packing requirements of surfactant head group and chains [23].

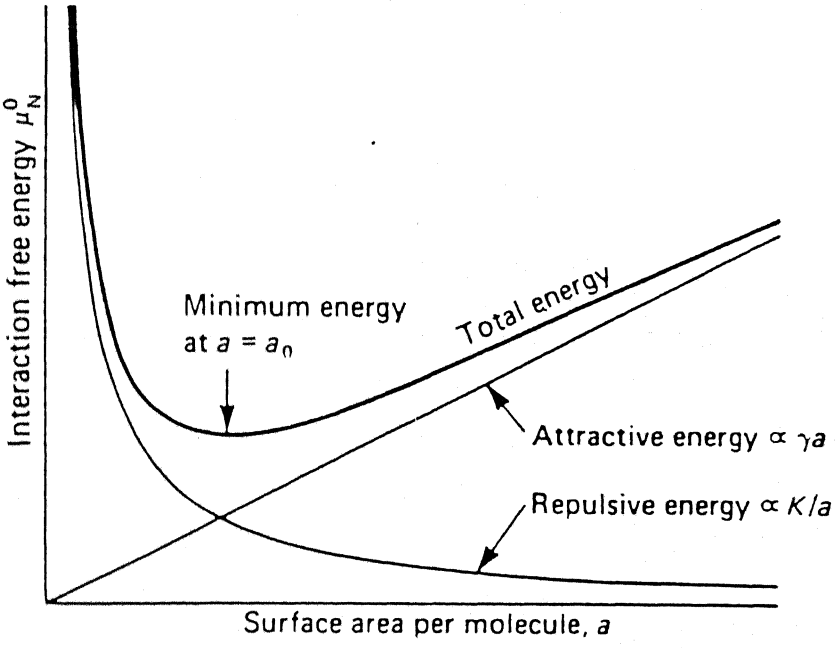


Figure 2.3 Attractive and repulsive interactions occurring in the interfacial head group region of amphiphilic structures. a_0 is the optimal head group area [24].

Chapter 3

THEORETICAL CONSIDERATIONS :

3.1 Flux through the membrane :

The water flux through the porous membrane can be describe by Darcy's law which state that the flow rate is directly proportional to applied pressure gradient;

$$J = \frac{1}{A}\left(\frac{dv}{dt}\right) = \frac{\Delta P}{\mu_m R_m} \tag{3.1}$$

where R_m is the membrane intrinsic hydraulic resistance. It is function of pore size, tortuosity, membrane thickness and porosity as follows;

$$R_m = \frac{8\tau\delta}{\epsilon a^2} \tag{3.2}$$

Since ultrafiltration membranes are plastic and can yield (compact) or creep under pressure, R_m is also a function of pressure history. Initial membrane compaction occur rapidly during startup, whereas long term compaction occures slowly during the operative life of the membrane itself. During membrane compaction, appiled pressure should be somewhat more than the maximum pressure at which the reading will be taken. During ultrafiltration of macromolecular solutes, the the linear relationship between flux(J) and pressure differential(ΔP) does not hold good. At that time, solutes get accumulated near the membrane causing permeate flow resistance to rise. But in our present studies there will be no concentration polarisation.

3.2 Osmotic Pressure model and Florey's equation :

From the concentration polarisation model, it is evident that the concentration of the solute on the membrane surface will be considerably higher than the bulk. This high concentration on one side of the membrane and very low on the other side creates an osmotic pressure difference($\Delta\pi$) which acts in opposition to the applied pressure (ΔP). So in equation 3.1, (ΔP) is now replaced by effective pressure differential ($\Delta P - \Delta\pi$),

$$J = \frac{\Delta P - \Delta\pi}{\mu_m R_m} \tag{3.3}$$

But this equation is still not correct. Macromolecular solutes may get adsorbed, can cause fouling and also form a distinct polarised layer, which is also not applicable for our cases. These phenomenon are accomodated by introducing the resistance due to adsorption term R_a and R_p, R_a being resistance due to adsorption and R_p that due to the formation of polarised layer. Therefore :

$$J = \frac{\Delta P - \Delta\pi}{\mu_m \left(R_m + R_a + R_p\right)} \tag{3.4}$$

3.3 Real and observed rejection :

Membrane rejection or the ability of the membrane to reject certain specific solute is defined as follows :

$$R_o = 1 - C_p/C_b \tag{3.5}$$

This equation involves the term C_p and C_b i.e. permeate concentration and bulk concentration which can be easily measured. So this rejection is called observed rejection. However, due to concentration polarisation, which is not in our case, the concentration at the membrane surface will be some what higher than the bulk. Rejection based on

membrane surface concentration is called real rejection and is defined as :

$$R_r = 1 - C_p/C_m \tag{3.6}$$

3.4 Thermodynamics of micelle formation :

Few attempts have been taken to clarify micelle formation from thermodynamic point of view. Sole problem lies on the precise description of the aggregated species. The free energy change for aggregation per mole of monomer referred to a mixed standard state:

$$\Delta\Phi_2^0 = RT\left[\ln X_2 - \{\ln(X_c - X_2)\}/\overline{n}\right] \tag{3.7}$$

The "mixed standard state" corresponding to a mixer of the individual micellar species in their respective standard states, X_2 is the mole fraction of the monomeric surfactant (X_1being the mole fraction of the solvent), X_c is the colligative mole fraction measured experimentally. If X_t is the total mole fraction of the surfactant, than average aggregation number, n can be determined from colligative measurements using the relation

$$\overline{n} = \frac{(X_t - X_2)}{(X_c - X_2)} \tag{3.8}$$

If we know X_2 from colligative property then with the help of above equations 3.7 and 3.8 we can calculate n and $\Delta\Phi_2^0$ as a function of concentration. On the other hand enthalpy of micellisation per mole of monomer for a non-ionic surfactant is related to the temperature dependent of the CMC by :

$$\Delta H_m = RT^2\left[\left\{\frac{\partial \ln X_2}{\partial T}\right\}_p - \left(\frac{1}{\overline{n}}\right)\left\{\frac{\partial \ln (X_c - X_2)}{\partial T}\right\}_p\right] \tag{3.9}$$

In practice, when alkyl chain length is consists of more than eight carbon atoms aggregation number soon becomes sufficiently large. So free energy for micelle formation becomes;

$$\Delta G_m^0 = RT \ln CMC \tag{3.10}$$

Where CMC is in mole fraction unit. When the aggregation number is large enough, then the micelle can be treated as a separate phase whose chemical potential is equal to the

standard chemical potential, since the mole fraction in this separate phase is equal to 1. These aggregates are in equilibrium with monomer in solution at a mole fraction euqal to the CMC, so that;

$$\mu_m = \mu_m^0 + RT \ln CMC \tag{3.11}$$

and $\mu_M = \mu_M^0$ (for micelle)

The standard free energy change on micellisation;

$$\Delta G_m^0 = RT \ln CMC \tag{3.12}$$

and the enthalpy of micellisation is

$$\Delta H_m = -RT^2 \left[\frac{\partial \ln CMC}{\partial T}\right]_p \tag{3.13}$$

Hence standard entropy of micellisation can then be calculated using the equations (3.12) and (3.13).

$$\Delta G_m^0 = \Delta H_m - T\Delta S_m^0 \tag{3.14}$$

3.5 Mechanism of micelle formation :

From fig. 3.1 it is clear that gradual decrease in stander free energy with increase in chain length [5]. It indicates, with increase in chain length hydrophobicity of the alkyl groups increases and hence increases the tendency of micelle formation. Further the micellisation is confirmed by high positive value of standard entropy of micellisation. Explanation for the high positive value of entropy as follows. Alkyl chains induce an increase in water structure around themselves is much, the same way as some nonpolar molecules such as noble gases can form clathrates with water. When micellisation starts that means alkyl chains aggregate in the form of micelle, the structured water around each chain reverts to ordinary bulk water with a considerable gain in entropy. If we put a nonpolar molecule into water a cavity in the water is created, which temporarily disrupts some hydrogen bonds. This breakage of hydrogen bonding is compensate by forming more hydrogen

bonds. This means, the water molecules around the nonpolar molecule are much more order than elsewhere in the bulk of the solution and thus gaining some entropy. So, nonpolar solute molecules are driven together in water not primarily because they have a high affinity for each other but because water bonds strongly to itself.

3.6 Solubilisation :

The term 'solubilisation ' means solubilise the organic solute in the interior of the micelle. Dissolution of hydrophobic materials into water form micelle. The interior of the micelle provides a hydrophobic environment in which nonpolar compounds can be accomodated. The addition of the hydrophobic solubilisate cause the micelle to grow until the number of ionic head groups per unit area of micelle surface is about the same as in the pure micelle. This implies, smaller molecules should be more readily solubilised than larger ones. If a co-surfactant is added, the curvature of the micelle surface can be increased and a larger quantity of hydrocarbon can be solubilised. Apparent solubilisation constant is defined;

$$K = \frac{X_0}{C_b} \tag{3.15}$$

where c_b is the concentration of unsolubilised organic solute in the bulk phase and X_0 the mole fraction of organic solute contained in he micellar species. K pertains to the equilibrium;

Organic solute + Surfactant micelle = Organic solute . Micelle

If the micelle aggregation number n is known, it is possible to multiply K by this number to obtain the mass action equilibrium constant for the reaction :

Organic solute $+A_n$ = Organic solute. A_n

Which represents the solubilisation of one molecule of the organic solute by a single micelle A_n. Here solubilisation of one molecule of the organic solute does not effect the micelle aggregation number $\overline{n}$.

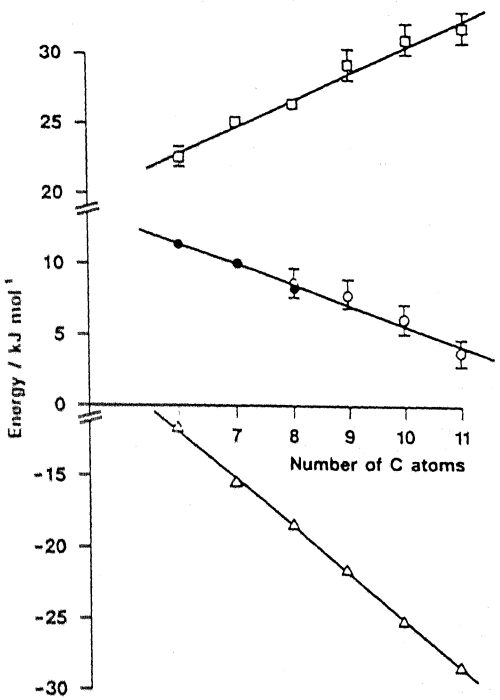


Figure 3.1 Thermodynamic quantities of micellisation for n-alkyl methyl sulphoxides at 296.7 K plotted against number of carbon atoms in the alkyl chain: (○) heat of micellisation (ΔH_m) from temperature dependence of the CMC; (●) heat measured calorimetrically; (Δ) standard free energy of micellisation (ΔG°_m); and (□) $T\Delta S^\circ_m$ [22].

Chapter 4

EXPERIMENTAL WORK :

4.1 Instruments and materials :

Membrane

Type : Permoinics

Nature : Flat disk, asymmetric, anisotropic, hydrophilic

Diameter: 0.076 m

MWCO : 1000 (pore size 0.59 nm)

Composition : Cellulose acetate material or hydrolysed cellulose acetate

pH : 2 to 10

Allowwable maximum temperature : $90°C$

Support : Highly porous, 150 to 300 micro meter

Skin : 0.1 to 0.5 micro meter

Sterilisation : By hydrogen peroxide or formaline or ethylene oxide

Suggested cleaning: By detergent with enzyme or 2.5 percentage hydrogen peroxide

Storage : 1 to 2 percentage formaline solution

Stirrer characteristics

Diameter of the stirrer : 0.056 m

Height of the stirrer from the membrane : 0.030 m

Sealing fluid : Sillicon grease

Stirrer motor

Type: Shunt, continuous rating

Supply : 220v,DC

Amperage : 0.85 amp

Horse Power : 0.125 Hp

RPM : 1450

Tachometer

Model : Toshniwal hand tachometer; type 630

Range : 30 to 50000

Accuracy (rpm): 1.333 between 30-150 : 44.44 between 100 500

1.333 between 300-1500 : 14.44 between 1000-5000

1.333 between 300-15000 : 14.44 between 10000-50000

Voltage stabiliser

Model : Automatic survo voltage regulator (Logic Control Pvt. Ltd)

Type : LLS/VRT-7/89

Current : AC, 50 cycles, 1 phase

Capacity : 2.5 kVA; Input-175-250v; Output 230 volt

Type of cooling : Air

VIS-UV Spectrophotometer : Sumadzu 160

Compressure

Type : VDE 0530

Supply : 220 volt, 1 phase, 50 Hz

Amperage : 2.6 amp

RPM : 1425

Wattage : 180 W

Unstrirred cell

Material of construction : SS-316

Total useful volume : 350 ml

Residual volume : 50 ml

Maximum operating pressure : 1000 kPa

4.2 Solutions :

Solutions of cetyl-pyridinium chloride (CPC) of molecular weight 340 and phenol (PhOH) of molecular weight 94.11 were prepared using distilled water. Cetylpyridinium chloride was obtained from Sigma Chemical Co., USA and phenol A.R. grade was obtained from Ranbaxy Laboratories Ltd., INDIA.

4.3 Design of experiments :

Experiments were designed so that the effects of three major independent variable i.e. bulk concentration, pressure differential and stirrer speed, can be properly understood on flux and rejection. During experiments, two variable are held constant (e.g. bulk concentration and pressure) while the third (stirrer speed) were varied to get exact picture of dependence. The levels for concentration were 10.2, 20.4 and 30.6 kg/m^3 while the pressure were varied as 207, 345 and 483 kPa and the stirrer speed level were 210, 300, 400 and 540.

4.4 Experimental Procedure :

After the experimental levels of variables were fixed, the experiments were conducted at the each set of variables. At first, a fresh porous membrane was placed on the porous support at the bottom of the cell as shown in fig. 4.1. The cell was then assembled. The main thing was then to allow for initial compaction of the membrane. For this purpose, the cell was pressurised with distilled water for at least 2 hours at 620 kPa (the pressure was higher than the highest level of pressure). Water flux was continuously measured during this period. Constancy of water flux beyond this time interval suggested no further compaction of the membrane. The constant water flux was note down to calculate membrane hydraulic resistance (R_m). Once the cell was assembled with cleaned and rinsed membrane the stirrer speed (for required rpm, for the stirred cell) was adjusted by regulating the voltage supply through a varier. The rpm was measured by techometer. To calculate flux, cumulative volume of water was collected in measuring cylinder, and time for this collection was also noted. Permeate concentrations of surfactant and organic solute were calculated from absorption values using VIS-UV spectrophotometer. After each run, the whole cell was ringed thoroughly with distilled water. The membrane was thoroughly washed and rinsed with distilled water at least one hour to remove any deposition. The water flux was then again checked to find quantitatively any adsorption resistance which act in series with membrane hydraulic resistance in the next run. This procedure was repeated for each set of operating conditions.

4.4.1 Measurement of concentration :

The optical densities (absorbancies) are additive, provided there is no reaction between the solutes. Therefore;

$$D_{\lambda_1} = D_{1,\lambda_1} + D_{2,\lambda_1} \tag{4.1}$$

$$D_{\lambda_2} = D_{1,\lambda_2} + D_{2,\lambda_2} \tag{4.2}$$

Where D_{λ_1} and *opticaldensitiesattwowavelengths*and the subscripts 1 and 2 refer to the two different wave lengths. The wave lengths are selected to coincide with the absorption maxima of the solutes. The absorption spectra of the two solutes should not overlap appreciably, so that substance 1 absorps strongly at wave length $\lambda_1$and weakly at λ_2, and substance 2 absorbs strongly at λ_2 and weakly at λ_1. Now $D = \epsilon.c.l.$ where is the molecular extinction co-efficient at any particular wave length, c is the concentration expressed in gmoles per liter, l is the thickness (length) of the absorbing solution expressed in cm. If l remain constant.

$$D_{\lambda_1} = \epsilon_{1,\lambda_1} c_1 + \epsilon_{2,\lambda_1} c_2 \tag{4.3}$$

$$D_{\lambda_2} = \epsilon_{1,\lambda_2} c_1 + \epsilon_{2,\lambda_2} c_2 \tag{4.4}$$

Solving the simultaneous eqations:

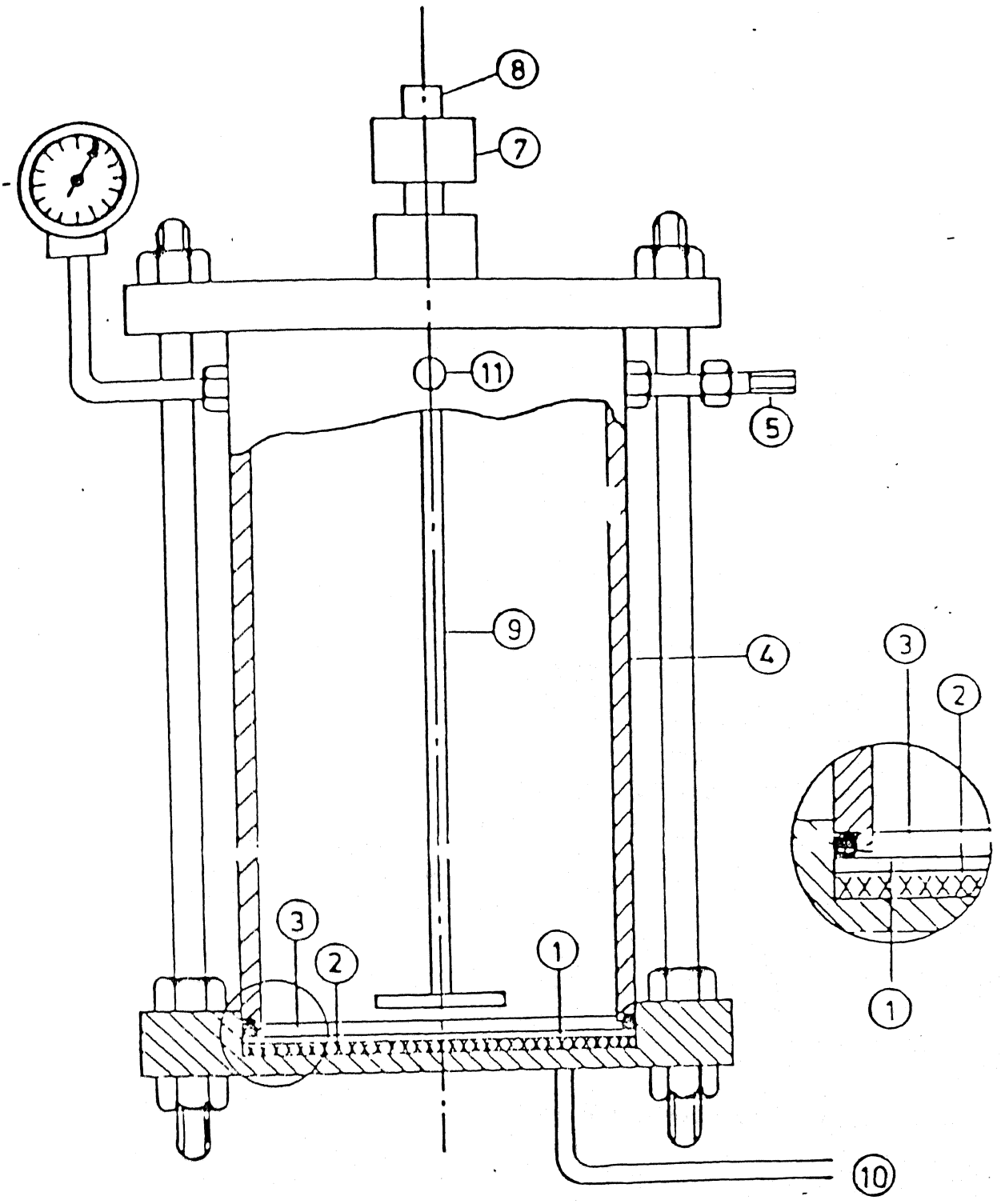
$$c_1 = \frac{\epsilon_{2,\lambda_2} D_{\lambda_1} - \epsilon_{2,\lambda_1} D_{\lambda_2}}{\epsilon_{1,\lambda_2} \epsilon_{2,\lambda_2} - \epsilon_{2,\lambda_1} \epsilon_{1,\lambda_2}} \tag{4.5}$$

$$c_2 = \frac{\epsilon_{1,\lambda_1} D_{\lambda_2} - \epsilon_{1,\lambda_2} D_{\lambda_1}}{\epsilon_{1,\lambda_1} \epsilon_{2,\lambda_2} - \epsilon_{2,\lambda_1} \epsilon_{1,\lambda_2}} \tag{4.6}$$

The values of the molecular extinction co-efficient and can be deduced from measurements of the optical densities of pure solutions of substances 1 and 2. By measuring the optical density of the mixture at wave lengths λ_1 and λ_2, the concentrations of the two components can be calculated. Here 1 is for cetylpyridinium chloride (CPC) and and 2 is for phenol (PhOH). Since the solute cetylpyridinium chloride and phenol have maximum absorbance at 259 and 270 nm therefore,$\lambda_1 = 259$ and $\lambda_2 = 270$. The UV-VIS spectrophotometer was used to calculate permeate monomer and organic solute concentrations.

4.5 RECOVERY OF SURFACTANT :

To make the process economically feasible, surfactant can be recovered and reused. Cationic surfactants can be recovered in an analogous fashion to anionic surfactants using either monovalent or multivalent counter ions. Cationic surfactant cetylpyridinium chloride could be recovered with chloride (monovalent anion) or chromate (divalent anion). In our present case 90-93 percent surfactant recovery is possible. The details of the recovery process is shown in fig. 4.2.



1. Membrane, 2. Porous Polyethylene Support; 3. 'O' Ring, 4. Cell Body, 5. Pressure Line Connector, 6. Pressure Gauge, 7. High Pressure Proved Sttuffien Box, 8. Adaptor, 9. Stirrer, 10. Sample Outlet, 11.Feed Sample Inlet

Fig. 4.1 Ultrafiltration Cell

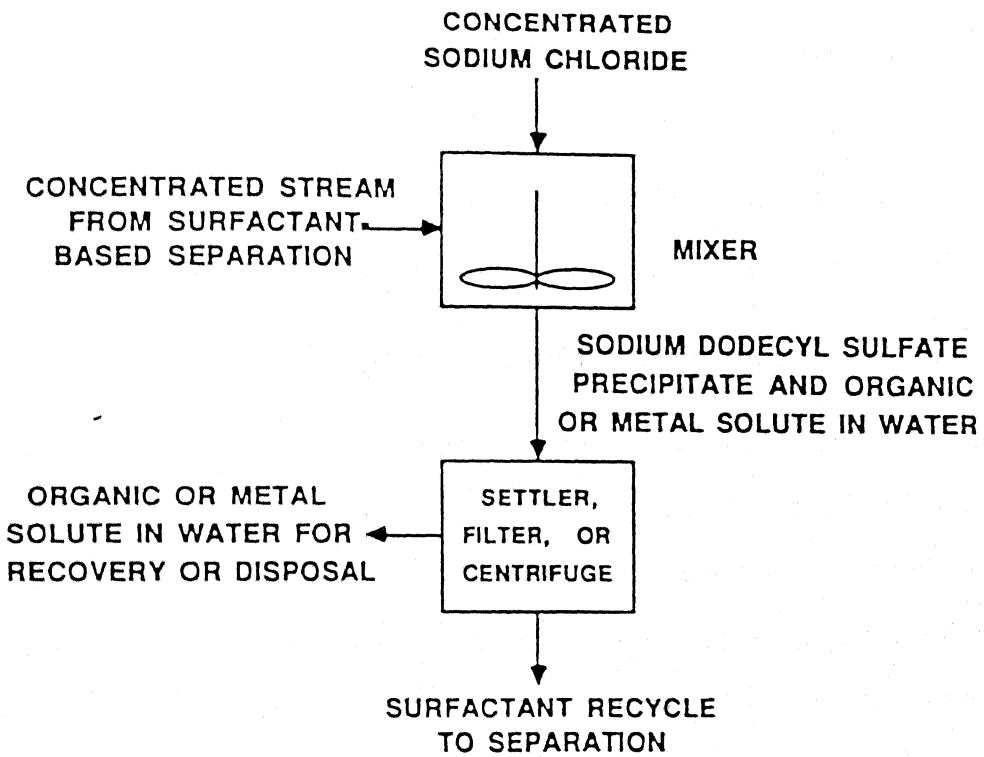


FIG. 42 Process flow diagram for recovery of sodium dodecyl sulfate using sodium counterion.

Chapter 5

RESULTS AND DISCUSSIONS :

5.1 Influence of operating variables on the permeate flux and rejection :

Three independent variables i.e. pressure differential, bulk concentration and stirrer speed were varied to study their effect on flux and rejection as a function of time.

5.1.1 Effect of pressure on permeate flux :

Fig. 5.1 shows the variation of permeate flux with time at different pressures, fixed bulk concentration ($= 30mM$) of CPC solution and under unstirred condition. The curves indicate that the flux remains constant with time . This leads us to believe that there is no significant concentration polarisation occuring during UF; otherwise flux would have shown a decline in flux. Further, it may be noted that these runs were taken under unstirred conditions. Hence, although flux remains constant but it is a depressed flux because of partial coverage of pores by micelles. This may be considered logical, as the micelles which have formed are of very high MW (46000). Thus, exhibiting no osmotic pressure or even extra any dynamic resistance against the flow. The figure also indicates that with increase in pressure flux increases. Obviously, with no significant concentration polarisation, with increase in pressure differential(Δp) flux increases linearly.

5.1.2 Effect of bulk concentration of the solution :

As the bulk concentration increases the permeate flux decreases. This fact is clearly indicated in figure 5.2 under unstirred condition. Osmotic pressure of the micellar solution increases with increase in bulk concentration, thus reducing the effective pressure differential ($\Delta p - \Delta \pi$). But again with increase in concentration, the dynamic extra resistance against flow was not observed which otherwise would have decreased flux with time. Further, the accumulation of large size micelles do not deter the passage of solute and monomer through void spaces; thus causing no extra resistance as well against the flow. However, these always be depressed flux with partial coverage of pores by micelles as discussed earlier.

5.1.3 Effect of stirrer speed on permeate flux :

The figure 5.6 clearly indicates the slight increase in flux with increase in stirrer speed. It must be stated here that if UF is carried out under unstirred condition, an instantaneous constant resistance build ups giving rise to constant flux (as discussed in section 5.1.1 and 5.1.2). However, if stirring is introduced, micelles positions on membrane surface get disturbed and they keep changing their position. Such action is more vigorous with increase in stirrer speed. This leads to higher flux in higher rpm. Further, to add that micelles hydrodynamic radius is around 6 times larger than monomeric surfactant [4].Hence, under stirred conditions membranes pores coverage by them is quite logical, because of attractive force between micelles and membrane. This phenomena has been explicitly further depicted in fig. 5.4 and Fig. 5.5 shows the effect of feed side CPC concentration under both stirred and unstirred conditions. It was observed permeate concentration increases with increase in feed concentration under unstirrer conditions. The rate of which is higher at higher feed concentration. This may be explained due to the fact that micelle when they move towards membrane in unstirred condition make a porous layer on the membrane surface. This layer make a local concentration gradient with the permeate

side. Due to this concentration gradient CPC moves at a firster rate to the permeate side resulting higher concentration. The probability of making porous layer is higher for high CPC concentration. From fig. 5.5 it is further observed that under stirred condition, there is practically negligible increase in permeate concentration upto 200 mM feed concentration; beyond which there is an exponential rise in permeate concentration. Explanation of these behavior is similar as has been above. However, it may be further attributed that upto 200 mM of feed concentration stirring at 540 rpm is sufficient enough to disturb micelles position from surface. Hence, losely bound monomer on micelle surface are not being to be present at the surface and hence no permeation of them. Whereas beyond 200 mM effect of stirring is lost wih respect to the available membrane area and number of micelle formed. These trends have been replotted in fig. 5.7 in terms of percentage rejection of CPC against feed side CPC concentration as function of pressure. Obviously, as permeate concentration increase percentage rejection decreases; hence inverse trends have been observed as compare to fig. 5.7.

5.2 Influence of surfactant concentration on solute consumption :

Fig. 5.6 shows the percentage consumption of phenol which increases with increase in feed CPC concentrations. For the three different pressures, the consumption pattern is observed to be similar. From these curves it is also clear that there must be an optimum surfactant/solute ratio in which efficiency of MEUF will be maximum; which, incidentally, for our case is around 30. Further, this value of 30 seems to be independent of pressure. It is also obvious from the curve that MEUF efficiency decreases with increase in pressure. This is because with increase in pressure solute containing capacity of the micelle decreases. Hence, one can conclude for effective removal of organic solute lower pressure region are advisable. Explanation for other behaviours have already been discussed earlier.

5.3 Mathematical model for the development of concentration :

5.3.1 Profile within the micelle :

It was observed experimentally that organic solute can easily be removed from aqueous streams using MEUF. However, their quantitative estimation could only be done by experiments. Lots of research has been carried out to study various aspects of MEUF [2]. However, there is practically no information available for the quantitative estimation of solute consumption in MEUF. In the present work, it was our objective to find the solute distribution within micelle in order to predict the solute consumption from bulk of solution, once it comes to the surface of the micelle. This may further provides to estimate the solute containing capacity of the micelle, through the development of the concentration profile within the micelle. Inspired from a work of the influence of co-solubilisate within the micelle [3], the present work has been taken up. The role of hydrophobic co-solubilisates such as cyclohexane and carbon tetrachloride for the removal of hydrophilic compound by MEUF depicts the movement of solute within the micelle as shown in fig. [5.8].

In order to develop simple however realistic model the following assumptions were taken :

1. The micelle formed is spherical, since for anionic surfactants the electrostatic repulsion between adjacent head groups results in a large value of a_0. Attractive and repulsive interactions occuring in the interfacial head group region of amphilic structure is shown in fig. 2.3 [5], a_0 is the optimal head group area.

2. Aggregation number is not changing during the period of time. Since, surfactant monomer rapidly join and leave micelle, whose aggregation number represents only an average over time and taken as constant.

3. The diffusion of solute is only due to polar and nonpolar interaction.

4. Diffused solute front is moving similar to the reaction front similar to a gas-solid reaction as in unreacted core model, as shown in fig. 5.8.

5. Constant physical properties of the micelles and the solute during experimentation.

6. Distribution of solute in stern layer is negligible. Since, for both cationic and anionic surfactants have such a strong affinity for water that they spaced out themselves to allow as much water as possible. Therefore, stern layer may e assumed to be polar in nature.

7. No reaction between surfactant and solute molecules.

8. Process is instantaneous.

9. Solute distribution is symmetrical with respect tc θ and Φ as in fig. 5.9.

The equation of continuity in spherical co-ordinate (for constant density and viscosity)

$$\frac{\partial c}{\partial t} + \left(v_r \frac{\partial c}{\partial r} + \frac{v_\theta}{r} \frac{\partial c}{\partial \theta} + \frac{v_\phi}{r \sin\theta} \frac{\partial c}{\partial \phi} \right)$$

$$= D \left(\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial c}{\partial r} \right) + \frac{1}{r^2 \sin\theta} \frac{\partial}{\partial \theta} \left(\sin\theta \frac{\partial c}{\partial \theta} \right) + \frac{1}{r^2 \sin^2\theta} \frac{\partial^2 c}{\partial \phi^2} \right) + R \qquad (5.1)$$

Considering no reaction between surfactant and solute molecules and solute distribution to be symmetrical with respect to and coordinates of the spherical micelle as shown in fig. 5.9, equation 5.1 reduces to :

$$\frac{\partial C}{\partial t} = D\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial C}{\partial r}\right)\right] \tag{5.2}$$

Further if the process is assume to be instantaneous equation 5.2 after integration becomes :

$$r^2\frac{dC}{dr} = K_1 \tag{5.3}$$

$$C(r) = -\frac{K_1}{r} + K_2 \tag{5.4}$$

BC's at $r = r_0$, $C(r) = 0$

and $r = R$, $C(r) = C_{\max}$

where $H = \frac{C_{\max}}{C_p}$

In corporating this boundary conditions 5.4 is solved to provide the concentration profile as :

$$C(r) = \frac{HC_pRr_0}{(R - r_0)}\left[\frac{1}{r_0} - \frac{1}{R}\right] \tag{5.5}$$

In order to obtain an average concentration of the solute in the micelle for the quantitative estimation of solute consumption equation 5.5 was integrated between r_0 to R to obtain average concentration of the solute as :

$$\overline{C} = \frac{\int_{r_0}^{R} 4\pi r^2 C(r)\, dr}{\frac{4}{3}\pi(R^3 - r_0^3)} \tag{5.6}$$

Substituting equation 5.5 in 5.6 and after arrangement and simplification the average concentration was obtained as :

$$\overline{C} = \frac{HC_p}{2}\left[\frac{2-\left(\frac{r_0}{R}\right)-\left(\frac{r_0}{R}\right)^2}{1-\left(\frac{r_0}{R}\right)^3}\right] \tag{5.7}$$

The detail derivatives are available in appendix 1.

5.3.2 Analysis of the results of the model :

The model to obtain the average concentration of solute within micelle, given by equation 5.7, was used to estimate equilibrium parameter H, or maximum concentration C_{max} in the micelle phase as a function of micelles mole fraction (Φ_s) in the bulk phase, initial bulk concentration C_0 and permeate concentration C_p. The hydrodynaic radious of $R(2.5\ nm)$ for CPC micelle is obtained from literature [4]. The value of alkyl chain lengths about $2.45\ nm$ [18] (appendix 2).

Material balance for a unit volume.

The solute mass balance is obtained as:

$$C_o = C_p + \Phi_s\overline{C} \tag{5.8}$$

Therefore, by substituting the value of $r_0/R(=0.02)$ in eqation 5.7 one can obtain

$$\overline{C} = 0.9898HC_p \tag{5.9}$$

From 5.8 and 5.9 one gets :

$$C_0 - C_p = 0.9898\Phi_s HC_p \tag{5.10}$$

and after simplification :

$$H = \frac{1.0103}{\Phi_s}\left(\frac{C_0}{C_p} - 1\right) \tag{5.11}$$

5.3.3 Equilibrium parameter

Fig. 5.10 depicts concentration profile within the micelle,which has been plotted from equation 5.5. It is interesting to observe that as the pressure on the bulk solution increases during ultrafiltration, average solute concentration within micelle decreases. This indicates a decrease in H value with increase in pressure. Decrease in H value with increase in pressure may be explained from the behavior of the micelles. It may be assumed that with the increase in pressure, the micelles become compact there by losing its solute containing capacity. Another observation of fig. 5.10, leads us to understand that there is a drastic reduction of solute concentration near ere centre of the micelle. Therefore, it may be assumed that with increase in hydrodynamic radius of the micelles, solute containing capacity of the micelle increases. From fig. 5.11 it is clear that when surfactant concentration increases with respect to PhOH, there is small increase in H value. This may be attributed to the fact that with increase in CPC concentration, micelle concentration increases. Therefore, with increase in micelle concentration, the solute containing capacity of the micelle will also increase. As explained earlier, this may lead to decrease in permeate concentration of the solute and hence leads to decrease in unsolubilised solute concentration in the feed side. Lower values of C_p give rise to higher values of H.

5.3.4 Solubilisation constant :

Solubilisation constant K is plotted against mole fraction of phenol within micelle, as in fig. 5.12. The curves show that for a particular operating pressure, K increases with increase in solute mole fraction within the micelle. This is obvious as solute mole fraction within micelle increases, the solubility of solute in micelle phase also increases; since K is the reflection index of solubility of the solute within micelle, so it will increase. When the pressure of the system is increased the solute containing capacity the solute containing capacity of the micelle decreases. This phenomenon has already been discussed earlier.

5.4 CONCLUSIONS :

Based on the experimental studies carried out for MEUF and the theoretical development of a concentration profile within micelle the following conclusions may be drawn.

1. Constant flux was observed during an experimental run under constant applied pressure and bulk CPC concentration, suggesting negligible effect of concentration polarisation.

2. Increase in pressure increases the monomer and solute concentrations (carried by micelle) at the membrane surface, increases concentration of both solute and monomer in permeate.

3. Stirring during MEUF plays an important role in terms of disturbing the settle micelles on the membrane surface (also due to attractive forces); there by, improving permeate flux. However, the effect was found to be upto 200 mM of feed CPC concentration at 540 rpm.

4. Increase in pressure decreases the solute containing capacity of the micelles.Maximum solute consumption within micelles was also observed to be controlled by a optimum surfactant/solute ratio (30).

5. Theoretical development of the concentration profile within micelle suggested that there is drastic reduction of solute near the centre of the micelle. Maximum distribution of solute concentration present in the micelle was observed within 80micelle's radius from surface.

6. Experimental results were confirmed by theoretical model suggesting that as permeate concentration increases equilibrium parameter H decreases.

7. Recovery of surfactant made possible by adopting a standard procedure [17].

5.5 RECOMENDATIONS :

1. Experiments have performed by taking one solute and one surfactant, this could be done for other solutes and surfactants also.

2. The effect of temperature on solute consumption within micelle has not been studied in this work. This can be investigated further.

3. Experiments may be conducted for other pressure region also.

4. Investigation using different MWCO membranes may be explored.

5. The membrane separation may be investigaed in a continueous frame of reference. Which is actually suitable for the industries.

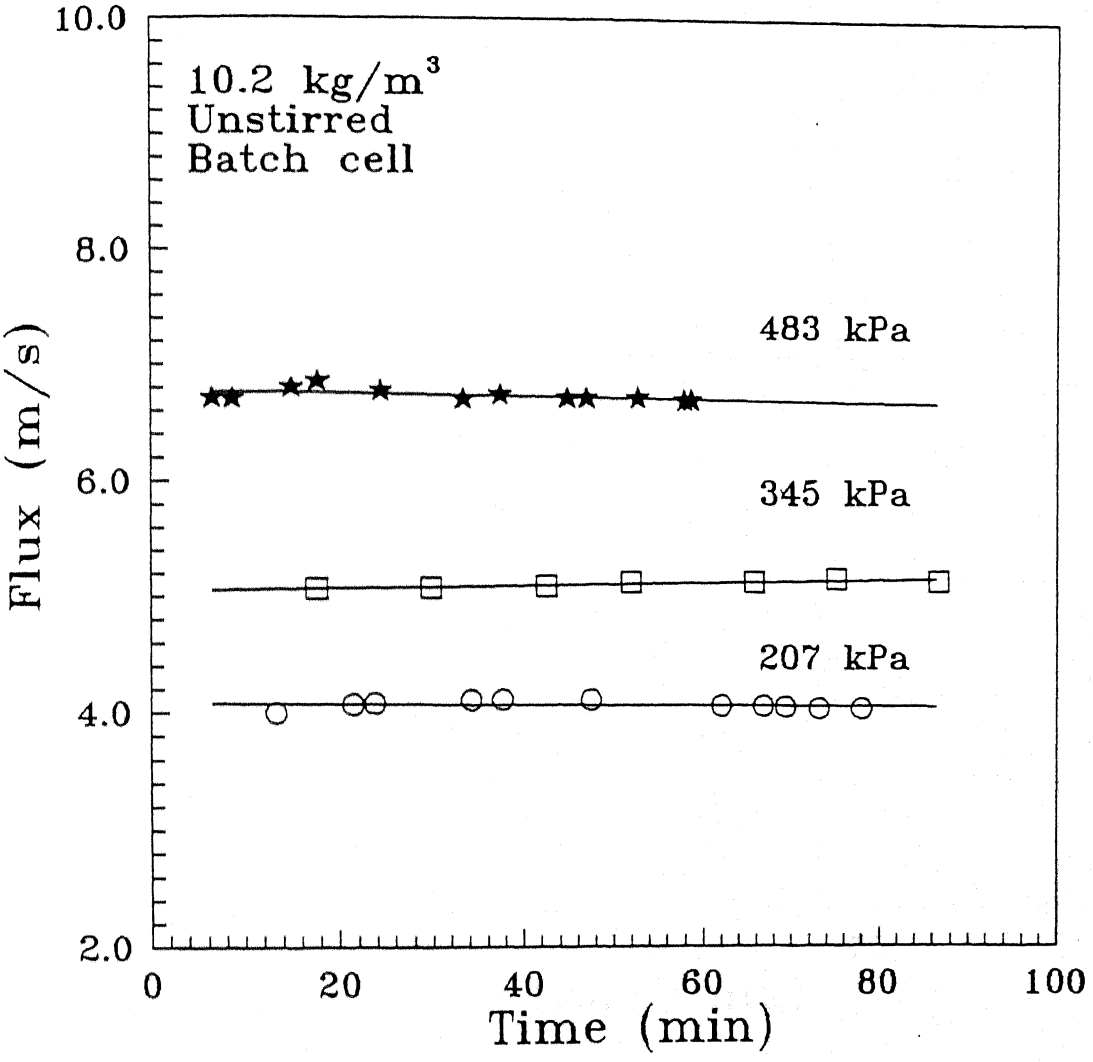


Fig. 5.1. Variation of permeate flux with time for CPC solution in unstirred batch cell.

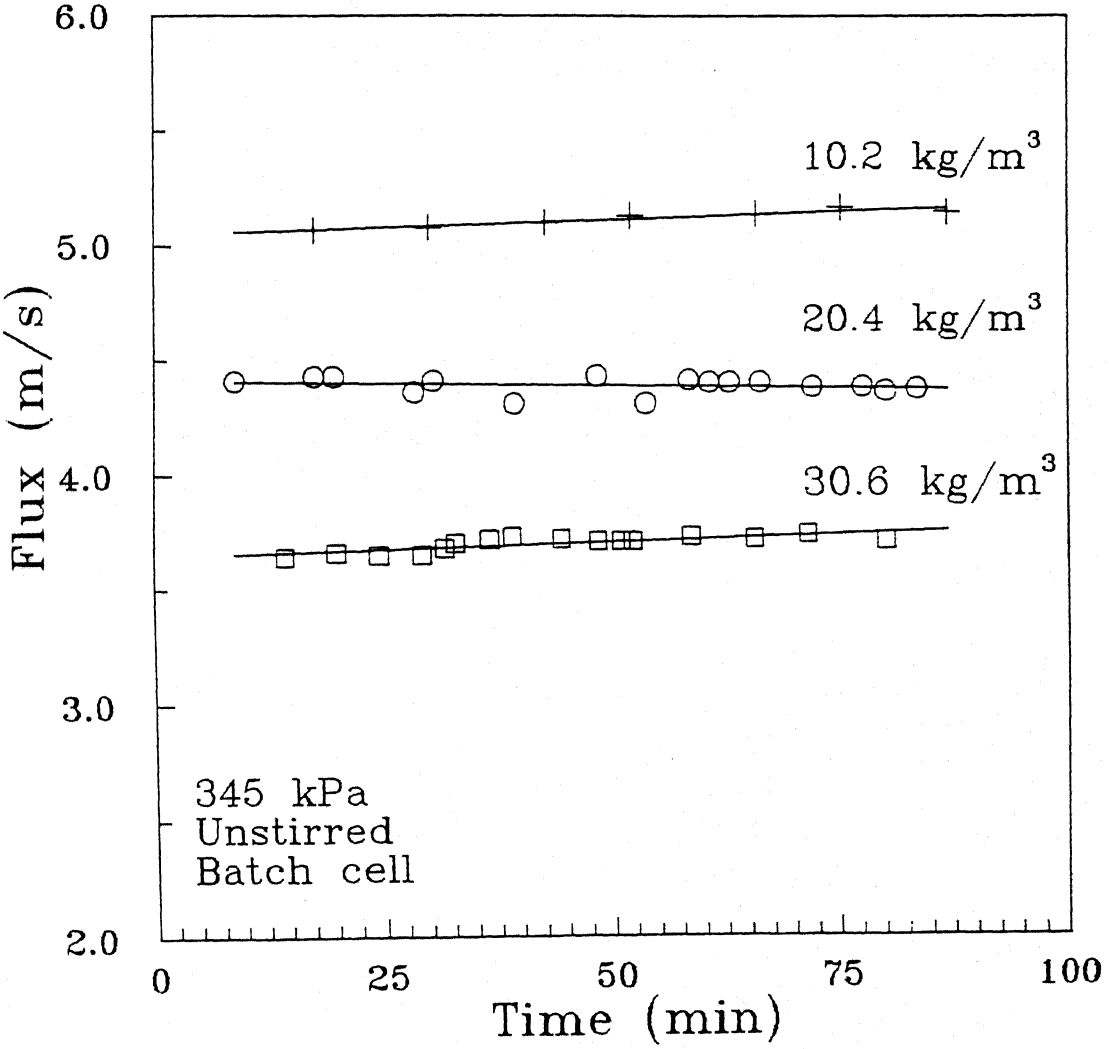


Fig. 5.2. Variation of permeate flux with time for CPC solution in unstirred batch cell.

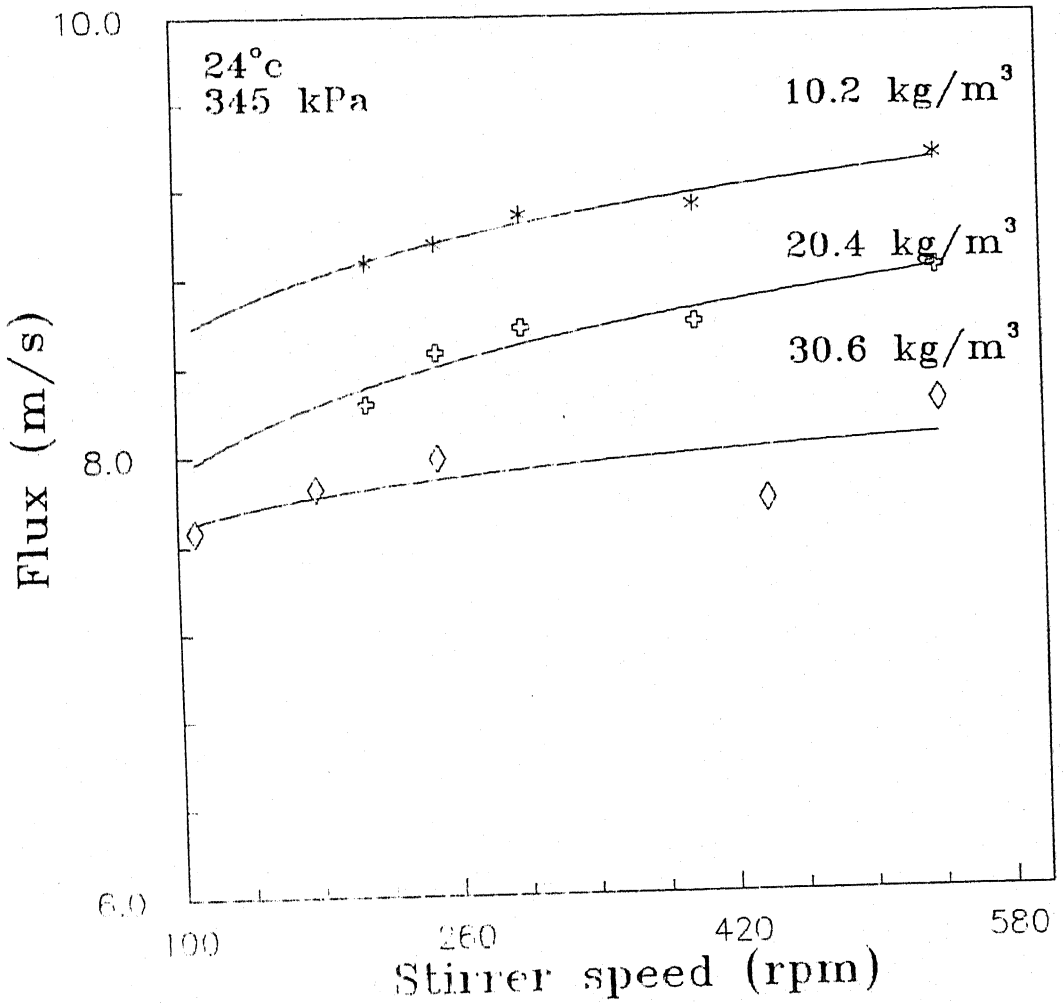


Fig. 5.3. Variation of permeate flux with stirrer speed for pure CPC solution in stirred batch UF

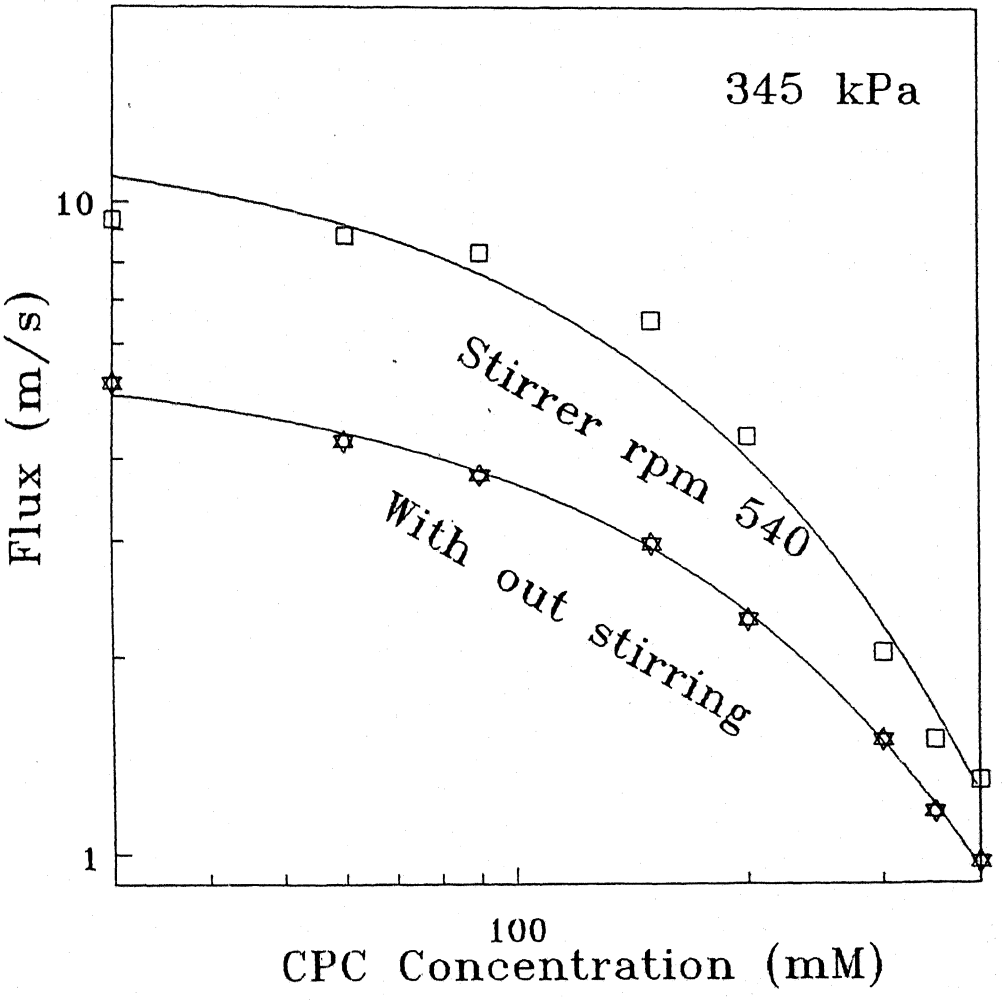


Fig. 5.4. Comparison of permeate flux with concentation between stirred and unstirred batch UF

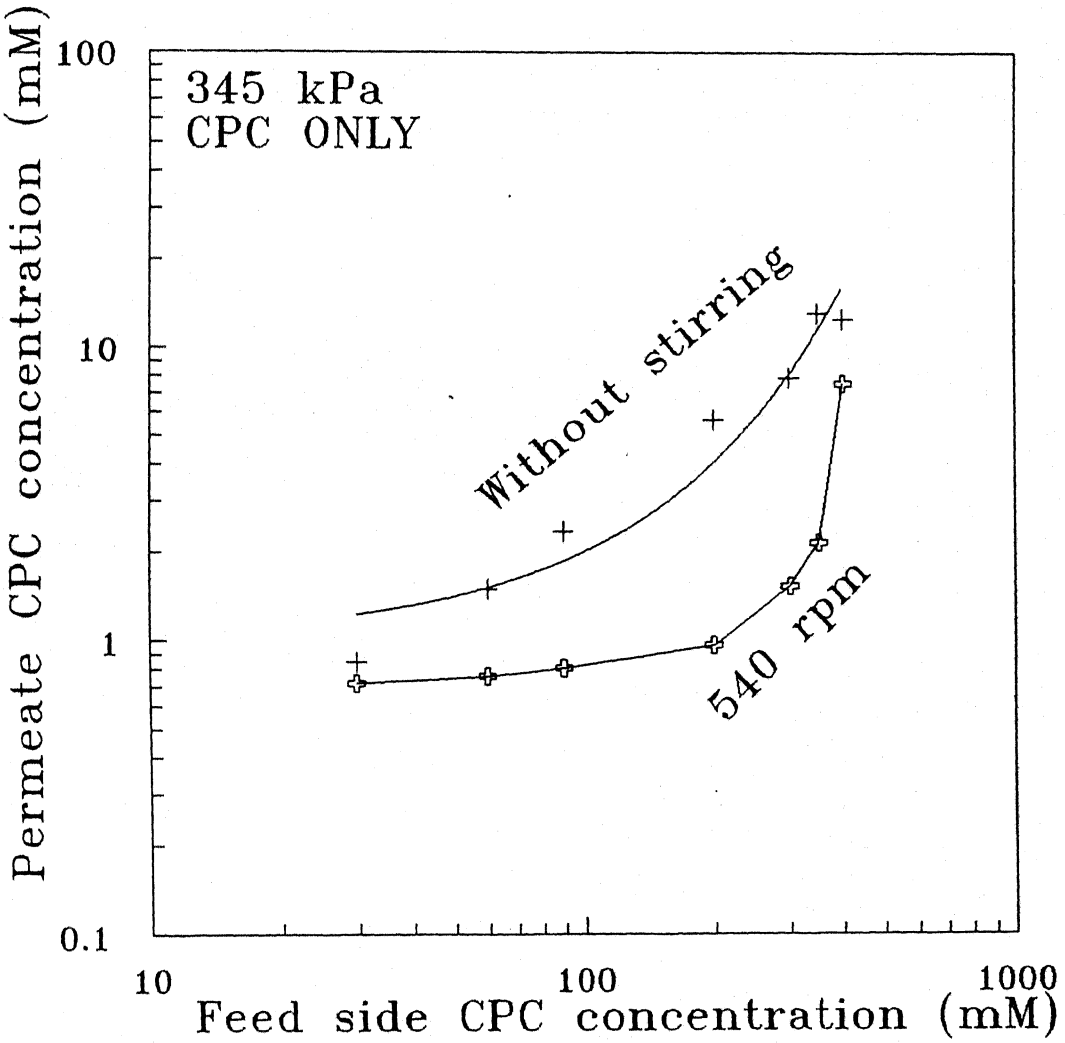


Fig. 5.5. Comparison of permeate concentration with feed concentation between stirred and unstirred batch UF

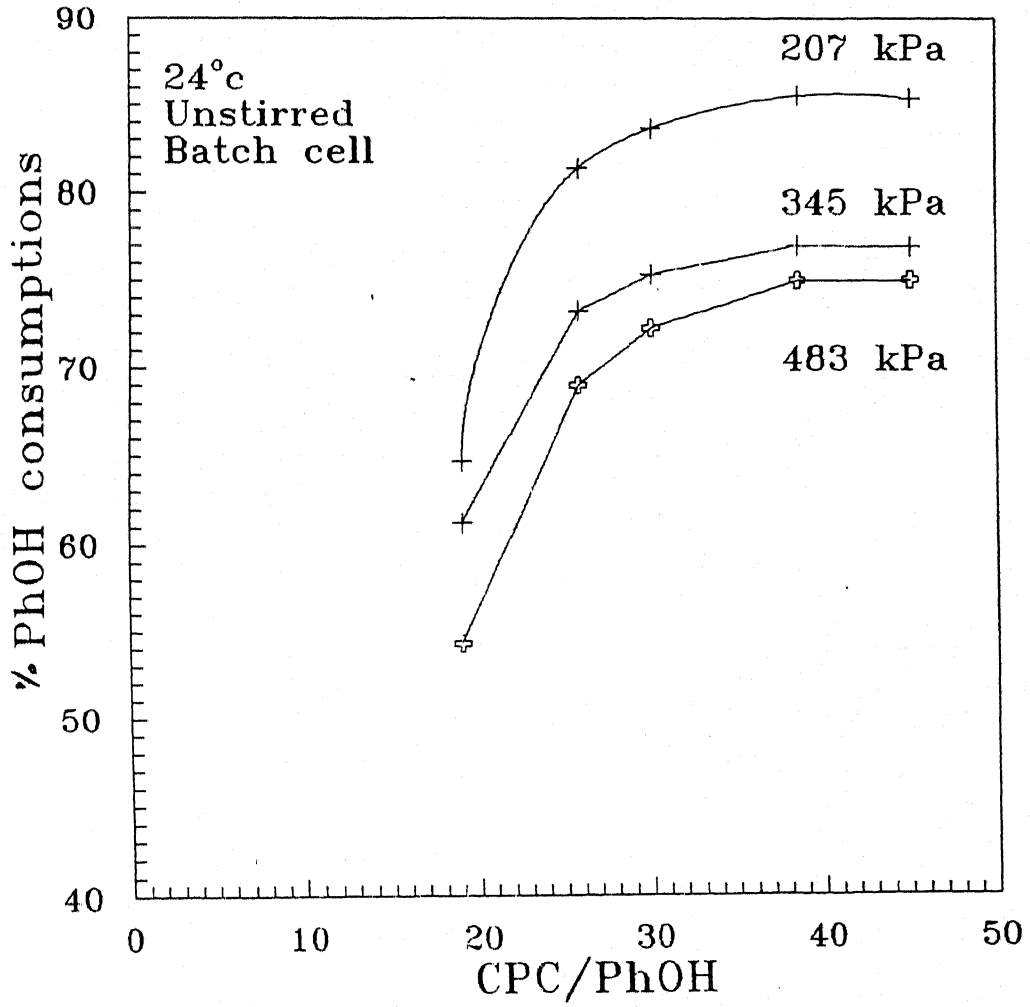


Fig. 5.6. Variation of phenol concsumption with CPC to phenol ratio in the bulk.

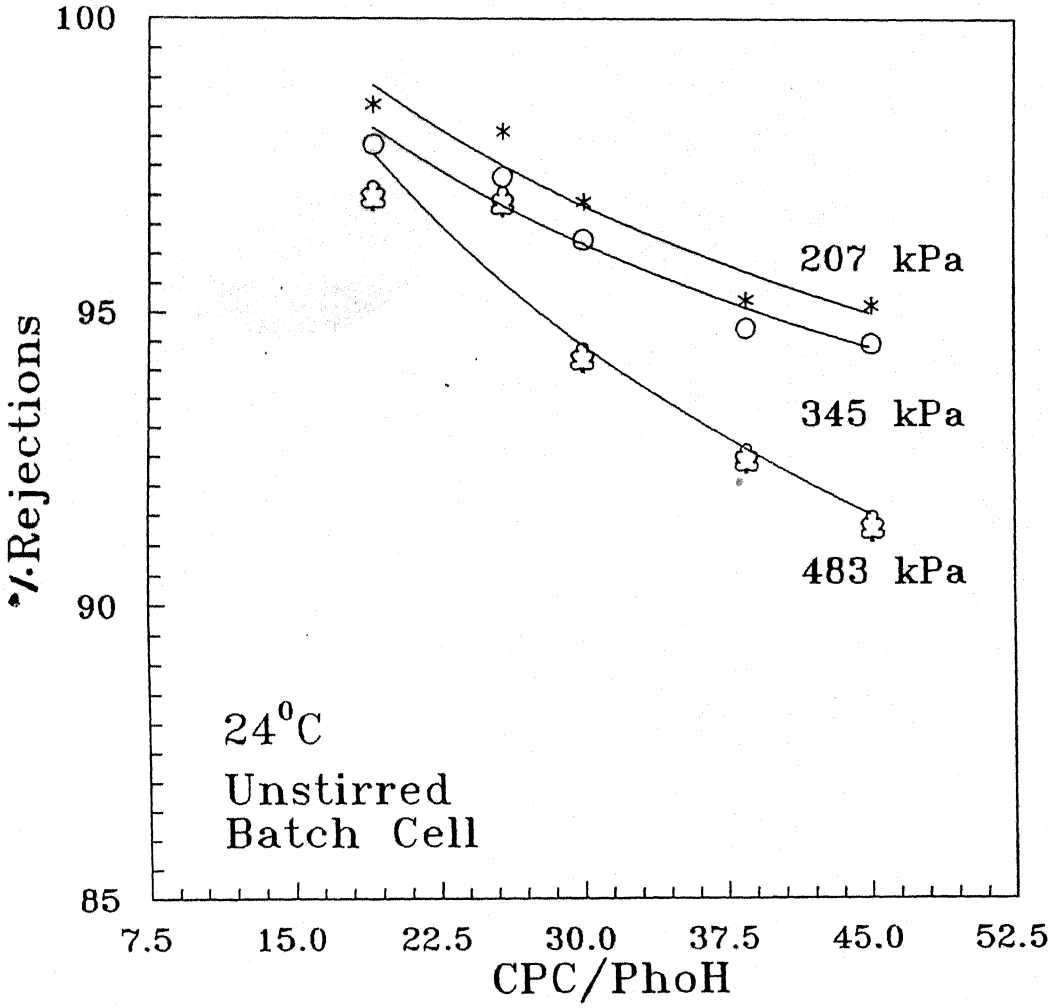


Fig. 5.7. Variation of CPC rejection with CPC to phenol ratio in the bulk.

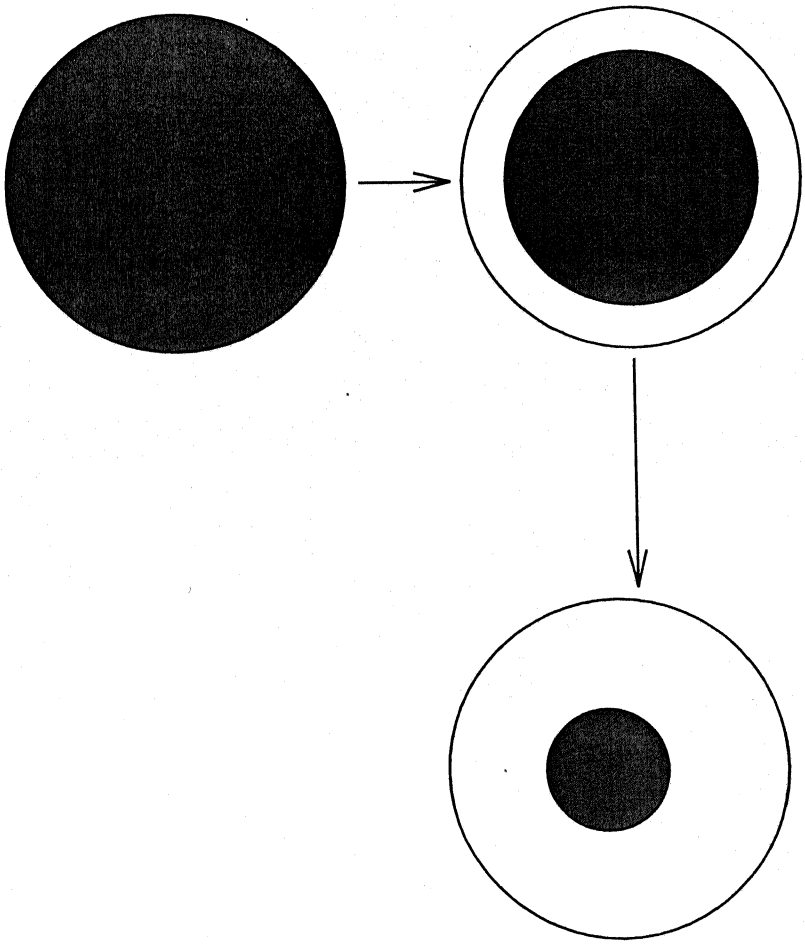


Fig. 5.8. Schematic of the diffused solute front movement in the spherical micelle.

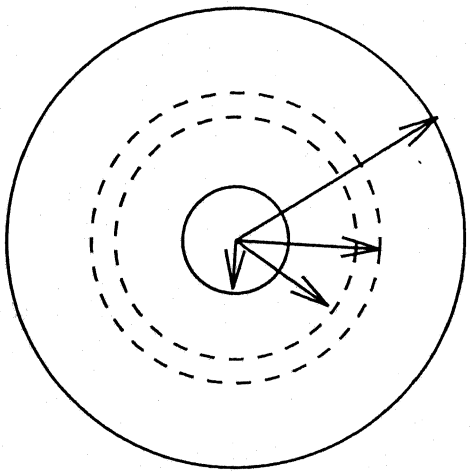


Fig. 5.9. Schematic of the choice of the coordinates in the spherical micelle.

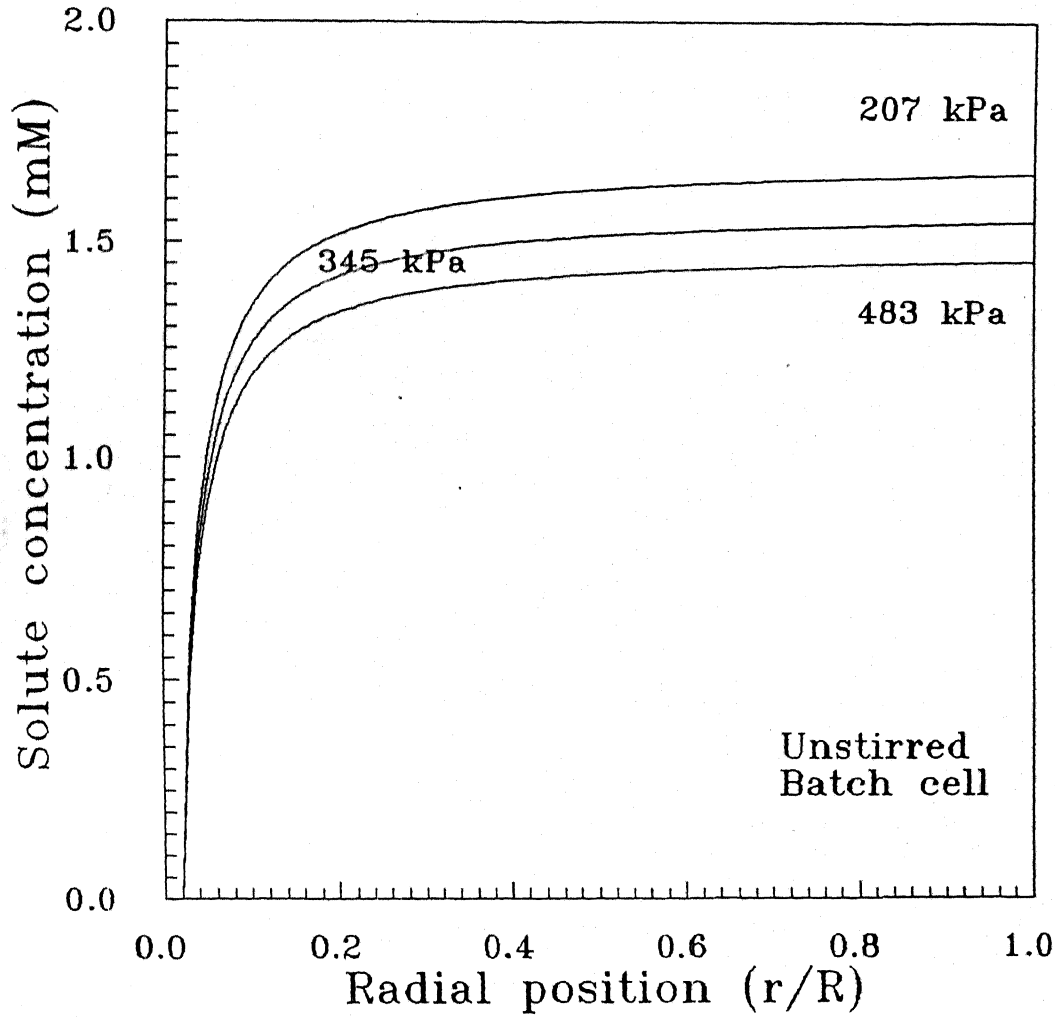


Fig. 5.10. Radial solute distribution within the micelle for different pressures in unstirred batch cell.

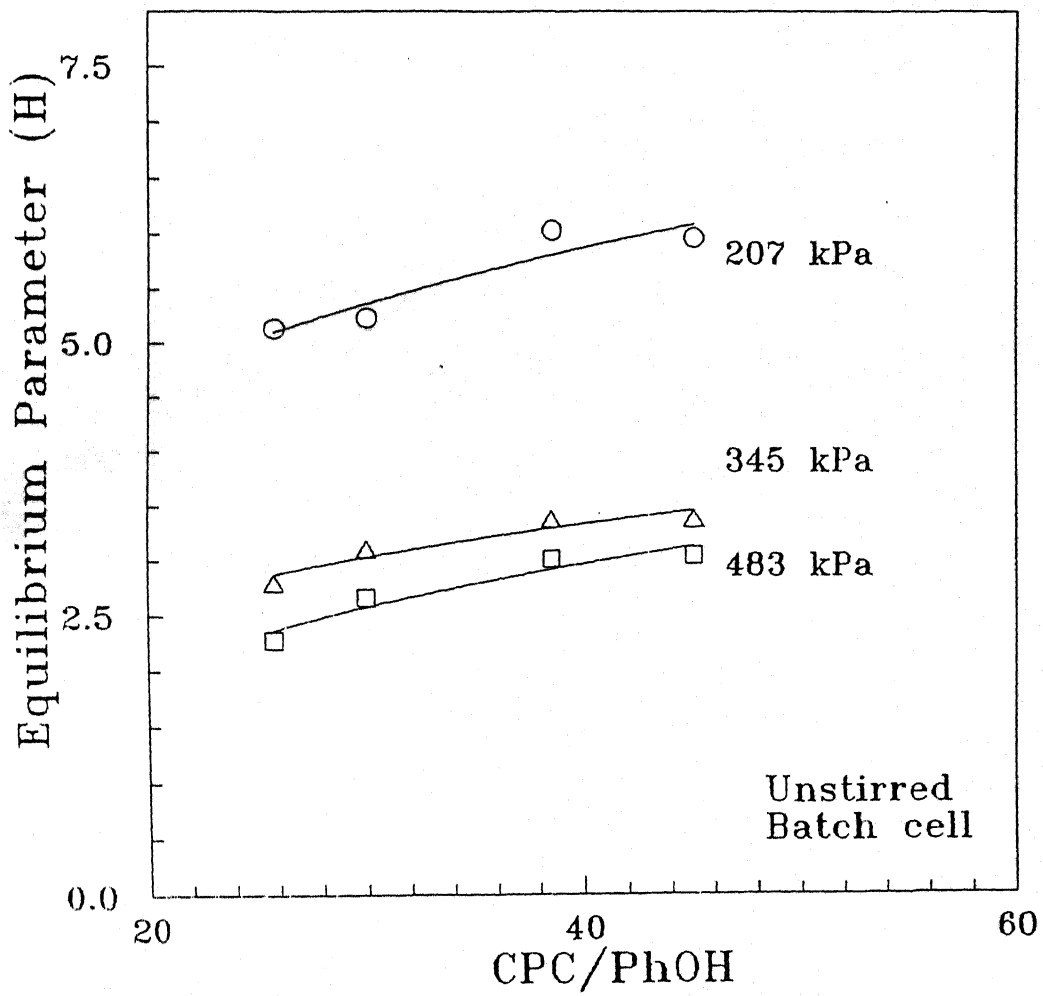


Fig. 5.11. Variation of the equilibrium parameter with CPC to phenol ratio for different pressures in unstirred batch cell.

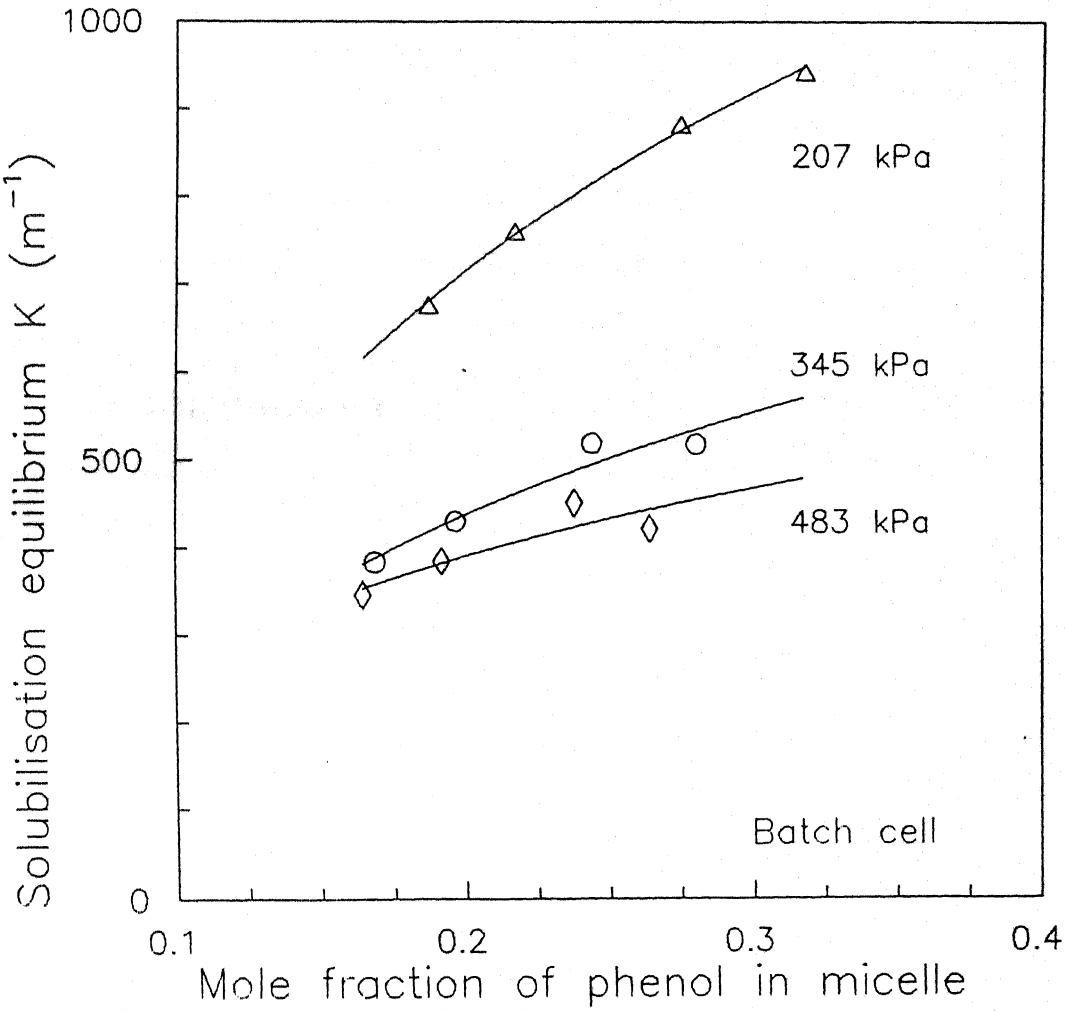


Fig. 5.12. Variation of solubilization equilibrium with mole fraction of phenol in micelle for different pressures.

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APPENDIX 1

$$\overline{C} = \frac{\int_{r_0}^{R} 4\pi r^2 C(r)dr}{4/3\pi\left(R^3 - r_0^3\right)}$$

$$= \frac{3HC_pRr_0}{(R-r_0)\left(R^3-r_0^3\right)} \int_{r_0}^{R} \left[\frac{r^2}{r_0} - r\right] dr$$

$$= \frac{3HC_pRr_0}{(R-r_0)\left(R^3-r_0^3\right)} \left[\frac{R^3}{3r_0} - \frac{r_0^3}{3r_0} - \frac{R^2}{2} + \frac{r_0^2}{2}\right]$$

$$= \frac{3HC_pR}{(R-r_0)\left(R^3-r_0^3\right)} \left[\frac{1}{3}\left(R^3 - r_0^3\right) - \frac{r_0}{2}\left(R^2 - r_0^2\right)\right]$$

$$= \frac{3HC_pR}{\left(R^3-r_0^3\right)} \left[\frac{1}{3}\left(R^2 + Rr_0 + r_0^2\right) - \frac{r_0}{2}\left(R + r_0\right)\right]$$

$$= \frac{3HC_pR}{6\left(R^3-r_0^3\right)} \left[2R^2 + 2Rr_0 + 2r_0^2 - 3Rr_0 - 3r_0^2\right]$$

$$= \frac{3HC_pR}{6\left(R^3-r_0^3\right)} \left[2R^2 - r_0R - r_0^2\right]$$

$$= \frac{3HC_pR^3}{6\left(R^3-r_0^3\right)} \left[2 - \frac{r_0}{R} - \left(\frac{r_0}{R}\right)^2\right]$$

$$= \frac{HC_p}{2} \left[\frac{2 - \frac{r_0}{R} - \left(\frac{r_0}{R}\right)^2}{1 - \left(\frac{r_0}{R}\right)^3}\right]$$

APPENDIX 2

$C\left(SP^3\right) - -C\left(SP^3\right) = 1.54\mathring{A}$

$N\left(SP^3\right) - -C\left(SP^3\right) = 1.47\mathring{A}$

Therefore, $R - r_0 = 15 * 1.54 + 1.47 = 24.57\mathring{A}$